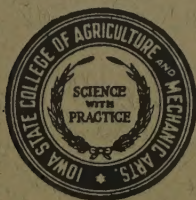


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IOWA STATE COLLEGE

# JOURNAL OF SCIENCE

*A Quarterly of Research*

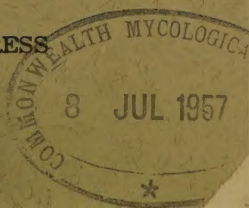


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ABSTRACTS OF DOCTORAL DISSERTATIONS

Accepted July 1, 1955 - June 30, 1956

These abstracts are arranged in alphabetical order by names of the authors. A footnote to each abstract carries the serial number of the candidate's dissertation, the date of acceptance by the Graduate College, the academic degrees held by him, his academic position (if any) in the several departments and research institutes of Iowa State College, and the name of the chairman of his committee.

The following summaries and indices may prove helpful to those interested in tabulations and to those who wish to examine groups of abstracts of theses in the same or related fields.

1. DOCTORAL DISSERTATIONS ACCEPTED JULY 1, 1955 - June 30, 1956 = 140  
Number of Doctor of Philosophy degrees conferred on candidates on whom first degrees were conferred by:
  - a. Institutions other than Iowa State College = 116.
  - b. Iowa State College = 24.

2. INDEX TO THESES BY DEPARTMENTS. Double indexing is used in those cases where two departments are jointly responsible. The departments are arranged alphabetically. Under each department are listed the names of the authors.

- Agricultural Engineering: 3.  
    Brakensiek, Hazen, Pedersen.
- Agronomy: 20. Adams, Allos,  
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    Grissom, Gross, Hutchcroft, John-  
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- Animal Husbandry: 8.  
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- Bacteriology: 3. Banwart, Hug, Ott.
- Botany: 11. Al-ani, Barrier, Dick-  
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    Andresen, Cammack, Giffen, Hsia,  
    Peterson, H.C., Wiley.
- Chemistry: 33. Atkinson, Baker,  
    Christian, Day, Douglas, Eidt, Eisch,  
    Ellingboe, Foos, Freeland, Gerow,  
    Gist, Goodman, Guter, Hedges,  
    Herrmann, Hollander, Minturn,  
    Naumann, Peterson, D., Reeder,  
    Renier, Rolih, Stevens, Summer,  
    Swayampati, Tollin, Wilder, Wolter,  
    Zaslow.
- Civil Engineering: 3.  
    Fung, Pedersen, Tabeling.
- Dairy Industry: 1. Brandsaeter.
- Economics and Sociology: 12. Anderson,  
    Brown, W.G., Cairns, Crecink,  
    Fischer, Ghormley, Kelley, Lanpher,  
    Mackie, McAlexander, McKee, Orazem.
- Electrical Engineering: 5. Christensen,  
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- Food and Nutrition: 3.  
    Garcia, Pudelkewicz, Yang.
- Food Technology: 1. Banwart.
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- Genetics: 3. Lasley, Sadanaga, Stadler.
- Geology: 1. Riggs.
- Home Economics Education: 1. McKinley.
- Horticulture: 1. Plaisted.
- Institution Management: 1. McKinley.
- Mathematics: 1. Yett.
- Physics: 9. Barson, Curtis, Gibson,  
    Hendrickson, Savage, Talboy,  
    Waddell, White, Whitsett.
- Poultry Husbandry: 2.  
    Donovan, Farnsworth.
- Statistics: 1. Brakensiek.
- Theoretical and Applied Mechanics: 1.  
    Hazen.
- Veterinary Hygiene: 1. Collier.
- Veterinary Pathology: 1. Ramsey.
- Vocational Education: 6. Collins, Easter,  
    Hanson, Heath, Lagomarcino, Thompson.
- Zoology and Entomology: 6. Elder,  
    Mitchell, Norris, Pattillo, Swailes,  
    Walstrom.

A graduate school can function only where there is adequate opportunity for research. The existence on the campus of Iowa State College of six research institutes, well integrated into the college programs is in large measure responsible for the growth of the graduate work. These institutes have frequently assumed the responsibility of providing research facilities necessary for the doctoral candidates in their respective fields. It is obvious that these institutes carry on a significant part of their research by use of workers who are in a sense apprentices in research. Under the name of each institute is given the total number of theses for which research facilities were afforded, and an alphabetical list of the authors of sponsored theses.

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##### Engineering Experiment Station: 3.

Hsia, Nolte, Riggs.

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Hanson.

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A RAINFALL SIMULATOR AND THE ERODIBILITY OF SOME IOWA SOILS<sup>1</sup>John E. Adams<sup>2</sup>

Department of Agronomy

A new type rainfall simulator and an infiltration cylinder were constructed and used to make measurements of erosion, runoff and infiltration in the field. The rainfall simulator delivered uniform drops averaging 5.56 mm in diameter from a height of approximately 1 meter on an area of 167.8 cm<sup>2</sup>. The kinetic energy delivered by each 5.56 mm drop in a 1 meter fall is equivalent to that developed by a raindrop 3.44 mm in diameter falling at terminal velocity, which is in the range of the median diameter drop size for a rain of 4 inches per hour intensity.

Infiltration measurements were made with the rainfall simulator on eight Iowa soils under a standard set of conditions so that the only known variables involved were the soil types. The soils were Clarion loam, Webster silty clay loam, Thurman loamy fine sand, Marshall silt loam, Ida silt loam, Monona silt loam, Grundy silty clay loam and Shelby loam. All soils studies were in the fall of the oat phase of a C-C-O-M rotation.

Ten plots, 3 x 3 feet, were randomly selected within an area, 9 x 21 feet, on each site. The vegetation was clipped at the soil surface within each plot and removed from the area. The brass infiltration cylinder, which was 6 inches in diameter and 6 inches deep, was installed near the center of each plot in such a manner that the soil surface was level. A sheet metal cylinder, 18 inches in diameter and 8 inches deep, was installed to a depth of 4 inches surrounding the infiltration cylinder. The soil area within both cylinders was cultivated to a depth of about 1/2 inch, and presoaked so as to be at field capacity at the time of measurement. A total of 2 inches of water was applied to each infiltration cylinder by the rainfall simulator at the rate of 4 inches per hour + 10 per cent. Runoff was caught in a trough which surrounded the infiltration cylinder and emptied into pint milk bottles. The pint milk bottles were changed at 5 minute intervals throughout the period of rainfall and the samples of runoff water and eroded material collected in them were taken to the laboratory for gravimetric determination of the rate and amount of water and soil which ran off. Infiltration was determined as the difference between rainfall and runoff. The runoff samples were also used to determine the rate and total amount of wash erosion caused by the 2 inches of rain applied. Splash erosion was determined by collecting and weighing the sediment which remained on the splash shield and in the runoff trough at the end of the rainfall.

Several physical measurements were made in the laboratory and field to determine various interrelationships. Air permeability measurements were taken just before rainfall, when the soil was at the field capacity moisture level, and at several time intervals after rainfall. Core samples were collected from the area next to the infiltration cylinder for moisture tension measurements. Aggregate stability and dispersion ratio were determined on soil samples collected from the area surrounding the infiltration cylinder.

The supplementary physical measurements indicated that, in general, the following factors were associated with erodible soils: 3.1 per cent or less of pore space drained at 60 cm; air permeability of 5.5  $\mu^2$  or less; 6.4 per cent or less of water stable aggregates > 2 mm; and 50 per cent or more of silt and clay with a dispersion ratio larger than 15.

<sup>1</sup>Doctoral thesis number 1764, submitted February 24, 1956.

Chairman of Committee, Don Kirkham, Department of Agronomy.

<sup>2</sup>B.S., University of Nebraska, Lincoln. M.S., *ibid*.

Graduate Assistant, Agricultural Experiment Station.

Correlations were calculated for the supplementary analyses vs infiltration and erosion as determined by the rainfall simulator. Highly significant positive correlations were found between the minimum infiltration rate and per cent pore space drained at 60 cm, 100 cm and  $1/3$  atmosphere of water tension. No significant relationship was found between the minimum infiltration rate and rainfall rate, dispersion ratio, water stable aggregates  $> 2$  mm, and aggregate mean weight diameter. A significant positive correlation was found between the maximum runoff rate and the rate of rainfall for all soils. When the data for the Thurman soil were omitted, the correlation was highly significant. A highly significant relation was found between the initial infiltration rate and per cent pore space drained by water tension of 60 cm, 100 cm, and 345 cm ( $1/3$  atmosphere).

No statistically significant relation was found between the dispersion ratio and wash erosion, or splash erosion. A highly significant negative correlation was found between wash erosion and percentage water stable aggregates  $> 2$  mm, and a highly significant positive correlation between wash erosion and rainfall intensity.

A significant negative correlation was found between splash erosion and per cent water stable aggregates  $> 2$  mm, and a significant positive correlation between splash erosion and rainfall intensity.

Based on the minimum wash erosion rate time interval, the eight soils studied could be divided into the following three groups: 1) erosion rate less than 0.1 ton per acre per hour (Thurman); 2) erosion rate, 0.95 to 1.3 tons per hour (Shelby, Ida, and Clarion soils); 3) erosion rate, 1.55 to 2.00 tons per acre per hour (Monona, Grundy, Webster, and Marshall soils).

Based on total wash erosion, the soils were divided into four statistically different groups. The Marshall with 1.20 tons per acre had the most wash erosion for 2 inches of rain and the Thurman with 0.03 tons per acre had the least. For both total erosion and splash erosion the soils could only be divided statistically into two groups, composed of Ida and Clarion as the least erodible, with the remaining soils falling into a broader group of higher erosion. The Thurman, although not significantly different from the other soils of the larger group in both splash and total erosion, was considered as a third group of splash and total erosion based on other physical factors.

Browning's rotation-soil factors and the relative soil erosion factors were calculated on the basis of total wash erosion and total splash erosion for the soils studied. Five erosion groups were established for both wash and splash erosion. The soils of this study fell in four of the five groups established for wash erosion and in three of the splash erosion groups. The Thurman soil was in the highest group of splash erosion for either factor and the Marshall in the highest group of wash erosion.

The present rainfall simulator appears to afford a satisfactory method of collecting erosion data for grouping soils for those times of the year when there is moderate soil moisture present and the rains are of short duration and high intensity. The apparatus could be modified to collect erosion data for longer, less intense rains by extending the infiltration cylinder to penetrate the B horizon and reducing the rainfall intensity. The present apparatus could also be used to study the effects of surface treatments or conditions on a given soil.

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ASSOCIATION OF CEPHALOSPORIUM ACREMONIUM CORDA  
WITH THE BLACK-BUNDLE DISEASE OF CORN<sup>1</sup>Hussain Yousif Al-Ani<sup>2</sup>

Department of Botany

The black-bundle disease of corn has been reported to be caused by Cephalosporium acremonium Corda and has been characterized by blackened vascular bundles, purple discoloration of the aerial vegetative parts of the plants, barren stalks, and multiple nubbins. The purpose of these studies was to investigate the association of this fungus with the black-bundle disease of corn and the method of plant and seed infection.

Six single crosses of corn and one inbred line were used in these investigations. The plants from the single crosses were grown in the field and greenhouse and inoculated with spore suspensions at different stages of growth through spiral whorls, stems, roots, and ears.

Whorl inoculations, made by dropping spore suspensions into the spiral whorls of the plants, did not produce any symptoms of the disease. Injection of a spore suspension into the stems of the plants with a hypodermic needle at three different stages of plant growth caused black bundles in the leaves, leaf sheaths, and stems of the inoculated plants.

Plants grown in the field and inoculated by hypodermic needle in the roots showed black bundle development in the stalks. Seedlings that were grown in pots in the greenhouse and inoculated two or four weeks after emergence, by pouring spore suspensions into the pots and at the same time damaging their roots, became infected, showing black veins and white streaks in the leaves and black bundles in the stems. Seedlings that were inoculated similarly, but without root damage, did not become infected.

The plants from the six single crosses that were inoculated through roots or stems and became infected did not show any significant variation from the check plants, similarly treated with distilled water, in purple discoloration, abnormal ear development, yield, or seed infection.

Plants from corn seed that were planted with a culture of C. acremonium or those grown from internally infected seed showed very little stalk infection.

The highest percentage of seed infection resulted from inoculating the corn ears at the tip three to six days after the appearance of the silks by forcing spore suspension within the husk. Relatively lower percentages of seed infection resulted when the ears were inoculated 14 to 20 days after silking. Spraying the silks with spore suspensions or injecting the shanks of the ears with the inoculum in the 1955 season did not produce significantly higher percentages of seed infection than similarly treating with distilled water.

Corn stalks from the inbred line, Illinois A, grown in the field during the 1954 and 1955 seasons developed blackened vascular bundles. Isolations made from these blackened bundles showed that very few of the bundles contained C. acremonium, Fusarium spp., or other fungi. The black bundle condition in this particular line was attributed to hereditary and environmental interaction. The blackening of the bundles started to show at the lower nodes and internodes of the plants about a week before tasseling. The discoloration of the bundles was due to deposition of a dark brown substance that appeared first in the phloem region of the vascular bundles, while the discoloration of vascular bundles in the plants that were infected with C. acremonium was due to a dark brown substance that appeared first in the xylem elements that contained the fungus.

<sup>1</sup>Doctoral thesis number 1743, submitted December 6, 1955.

Chairman of Committee, Charles S. Reddy, Department of Botany.

<sup>2</sup>B.S., Kansas State College, Manhattan. M.S., *ibid*.

Graduate Assistant, Agricultural Experiment Station.

Discoloration of the aerial vegetative parts of injured uninoculated plants of all the single crosses varied in intensity and location from one cross to another. When ears were removed, plants of single cross Hy x C103 produced the highest pigmentation on the leaves, while plants from the single cross Oh43 x C103 produced the lowest amount of discoloration.

Isolations from blackened bundles from corn stalks that had corn borer tunnels showed that C. acremonium was present in a high percentage of the stalks.

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## INFLUENCE OF INORGANIC NITROGEN ON THE INHIBITION OF SYMBIOTIC NITROGEN FIXATION<sup>1</sup>

Hazim F. Allos<sup>2</sup>

Department of Agronomy

Nitrogen absorption by a number of leguminous plants from the air and from added fertilizer was measured when varying quantities of fertilizer nitrogen were supplied to the plants. The legumes were grown in gravel-nutrient solution cultures equipped with a device for automatic irrigation. Mineral nutrients, sufficient for the plant needs, were added to the cultures at the beginning of the growth periods. Nitrogen was added at varying rates at weekly intervals. The legumes studied were sweet clover, alfalfa, Ladino clover, birdsfoot trefoil, and soybeans.

For the purpose of relating the nitrogen supplies and the extent of symbiotic fixation obtaining in the solution cultures to those obtaining in soils, brome grass, orchard grass, and Sudan grass were grown concurrently in the solution culture and in soil.

Yield increases resulted in all legumes from increases in the quantities of fertilizer nitrogen supplied to the legumes. Moreover, with the single exception of birdsfoot trefoil, the lowest rate of nitrogen addition resulted also in increases in nitrogen fixed from the air over that fixed where no nitrogen was supplied. The higher rates of nitrogen addition, with the exception of the case of soybeans, resulted in decreases in both the amount and proportion of nitrogen fixed. With soybeans the amount of fixation was highest at the highest level of nitrogen fertilization.

Under the conditions of the experiment, the symbiotic fixation mechanisms did not furnish sufficient nitrogen for maximum growth of the legumes. Added nitrogen tended both to increase yields and to replace the fixation processes.

Soybeans grew the most rapidly of the legumes studied, absorbed the greatest quantity of nitrogen and as a consequence fixed the most nitrogen in a 10-week growing period. Among the perennial legumes alfalfa exceeded both sweet clover and birdsfoot trefoil in total growth, nitrogen absorbed, and in nitrogen fixed in three cuttings over a twenty-two-week growing period.

Nitrogen fixation among the legumes was directly related to total production of dry matter. Alfalfa and birdsfoot trefoil were slower in becoming established than sweet clover and consequently fixed less nitrogen in the early stages of growth. Once established, however, alfalfa grew more rapidly than sweet clover and in consequence fixed more nitrogen.

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<sup>1</sup>Doctoral thesis number 1757, submitted January 10, 1956.

Chairman of Committee, W.V. Bartholomew, Department of Agronomy.

<sup>2</sup>B.Sc., Cairo University, Egypt. M.S., Iowa State College, Ames.

Graduate Assistant, Agricultural Experiment Station.



The influences of available nitrogen in replacing fixation were similar in all the legumes studied when considered from the standpoint of nitrogen applied in relation to the total nitrogen needs of the legumes. When the percentages of nitrogen absorbed coming from fixation were plotted against the ratio of the nitrogen applied over the nitrogen absorbed by the legumes, all of the levels of nitrogen nutrition for all of the legumes fell in a linear band. Extrapolation of the linear band to zero fixation indicated that additions of nitrogen slightly in excess of the maximum amount absorbed by the plants would completely inhibit fixation.

Recoveries of added ammonium nitrogen ranged from 76 to 94 per cent in the legume crops to from 79 to 97 per cent in the grasses.

Nitrate and ammonium ions from ammonium nitrate fertilizer were absorbed in about equal proportions by alfalfa, soybeans and Sudan grass, indicating that similar results in nitrogen uptake by legumes and grasses and similar replacements of fixation should be expected had a nitrate fertilizer been employed in place of ammonium.

The conclusion is reached that in soils containing from 0.2 to 0.3 per cent nitrogen, alfalfa and sweet clover normally fix from 60 to 75 per cent of the nitrogen absorbed. For Ladino clover and birdsfoot trefoil under the above soil conditions fixation would range between 25 and 60 per cent of the lower fixations occurring in the first growing season, particularly with the slow-growing birdsfoot trefoil.

#### FACTORS AFFECTING ACCEPTANCE AND USE OF FERTILIZER ON IOWA FARMS<sup>1</sup>

Marvin A. Anderson<sup>2</sup>

Departments of Economics and Sociology and of Agronomy

The objectives of this study were four-fold, 1) to characterize the Iowa fertilizer user and nonuser, 2) to ascertain and describe the fertilizer use practices in Iowa, 3) to determine the informational sources important in the acceptance and use of fertilizer, and 4) to determine the capital and tenure relationships with respect to fertilizer use. Interview schedules were elicited from 532 farmers in the state. The sampling design permitted unbiased estimates for each of nine soil areas in the state or any combination thereof.

Sixty-nine per cent of the farmers in Iowa had fertilizer use experience in 1952 or 1953; 62 per cent were users in 1953. Ten per cent of the users in 1952 did not fertilize in 1953. Tenant-landlord sharing arrangements, lack of capital and poor response were given as reasons for the discontinued use.

A fertilizer user could be characterized generally as having more capital, a larger farm, the benefit of more years of education, fewer years of farming experience and being somewhat younger than the nonuser.

Sixty-three per cent of the nonusers believed fertilizer was beneficial. Twelve per cent of the users either believed fertilizer was harmful or did not know what effect it would have on the soil.

Soil tests to determine fertilizer needs had been used by 38 per cent of the users and by 8 per cent of the nonusers.

<sup>1</sup>Doctoral thesis number 1755, submitted December 10, 1955.

Chairmen of Committee, Karl A. Fox, Department of Economics and Sociology and W. H. Pierre, Department of Agronomy.

<sup>2</sup>B.S., Iowa State College, Ames, Iowa. M.S., *ibid*.

Associate Director, Agricultural Extension Service.

One-fourth of the fertilizer users and over three-fourths of the nonusers were not able to identify the nutrient composition of a fertilizer grade such as 4-16-16.

Corn planting rates averaged 15,280 plants per acre for the fertilizer user as compared to 19,920 plants per acre for the nonuser.

"Other farmers" (neighbors, friends, and landlords, etc.) were the most frequently mentioned sources of information causing Iowa farmers to start using fertilizer. This was given by 57 per cent of the farmers. Mass media, the next most frequently mentioned source accounted for 20 per cent. The others, in order, were: personal experience, 9 per cent; field days, demonstrations and meetings, 8 per cent; dealers and salesmen, 4 per cent. The influencing source mentioned was significantly dependent on the operator's educational experience, years of fertilizer experience, years of farming experience, size of farm and capital position.

For information on a new fertilizer, 60 per cent of the farmers would look to Iowa State College, 12 per cent to dealers and salesmen, and 10 per cent to other agricultural agencies. The source selected was significantly dependent on educational status and tenure.

It is estimated on the basis of the sample that 54,600 tons of nitrogen, 95,000 tons of  $P_2O_5$  and 35,500 tons of  $K_2O$  were used by Iowa farmers in 1953. Although 62 per cent of the farmers used some fertilizer, only 21 per cent of the farm land received fertilizer treatment in 1953. Northern Iowa had the highest proportion of farm land fertilized.

Ninety-four per cent of the land fertilized in 1953 was in corn or small grain. Four-fifths of the  $K_2O$ , three-fourths of the N, and one-half of the  $P_2O_5$  were used on the corn crop.

The rates of fertilization as well as the grades of fertilizer used vary greatly among soil areas; however, the grades used reflected the general recommendations made by Iowa State College.

The average rates of application were 15, 27, and 10 pounds of N,  $P_2O_5$  and  $K_2O$ , respectively, per fertilized acre. The rates used per acre for nitrogen and potash were greatest on the corn crop, while the small grain crop received the greater application of  $P_2O_5$  per acre.

Hill or row fertilization for corn was used by about 75 per cent of the farmers in northeastern Iowa, while less than 5 per cent of the farmers used this method in western Iowa.

Total expenditures for fertilizer were only slightly less for tenant operators than by owner operators, the average amounts being \$1.58 and \$1.87 per acre, respectively. Tenant operators said they could profitably spend more money for fertilizer than owner operators. This estimated "most profitable" expenditure for fertilizer amounted to an average of \$534 for tenants and \$434 for owner operators. This was an increase of \$213 and \$91, respectively, over their 1953 expenditures. Lack of capital was identified as the most important limitation for optimum use although tenants also identified problems in the area of production planning (landlord and tenant) and in cost-sharing arrangements.

Tenant operators indicated they would use more fertilizer if (a) they owned the farm they operated and (b) the landlord would share costs in relation to crop-sharing arrangements. In 1953, where the landlord shared costs, tenants used 51 per cent more fertilizer than when costs were not shared.

Forty-two per cent of the tenants and 52 per cent of the owners indicated they would use more fertilizer if they had more capital. At the same time, although 81 per cent of the owners and 79 per cent of the tenants said they could borrow money for fertilizer, only 4 per cent of the owners and 6 per cent of the tenants actually borrowed money for this purpose in 1953.

When additional security was not required of the borrower, 19 per cent of the owner operators and 29 per cent of the tenant operators indicated they would use more fertilizer. If a repayment schedule could be timed in accord-

ance with crop returns, more fertilizer would be used by both owners and tenants, the average amounts indicated being \$172 and \$204, respectively.

The competition for capital among the various enterprises was suggested by both owner and tenant operators. When questioned how they would allocate an additional \$1000 in their farm business, tenants indicated they would use a greater proportion for livestock and farm machinery than for fertilizer. Repaying debts and reserves called for allocations almost as great as the \$165 allocated on an average for fertilizer. Owners indicated they would invest over twice as much for buildings as for fertilizer and they too would allocate nearly as much for repaying debts and building reserves as the \$131 they would invest for fertilizer.

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## RECOVERY OF URANIUM FROM SUPERPHOSPHATE<sup>1</sup>

Arthur W. Andresen<sup>2</sup>

Department of Chemical Engineering

Florida phosphate rock and the phosphoria formations of Idaho, Montana, Utah and Wyoming have a uranium content ranging from 0.01 to 0.02 per cent. The abundant domestic reserves and the relatively large tonnages of phosphate rock mined each year cause these low-grade uranium sources to be of great potential importance. Most phosphate rock is used for the production of normal superphosphate, which is made by acidulating the rock with sulfuric acid to get a form of phosphorus available to plant life. This study was undertaken to develop a method of recovering uranium during the production of superphosphate without destroying the plant nutrient value of the product.

A process was developed that is capable of recovering at least half of the uranium present in superphosphate. The process consists of a single step liquid-slurry extraction in which an organic solvent is mixed with freshly acidulated phosphate rock. A solution of 10 per cent octyl pyrophosphoric acid in kerosene is used as the solvent. A 10 minute extraction with as little as 0.24 lb of this solvent per lb of rock was capable of recovering uranium.

Two different acidulation-extraction procedures were studied. The first of these used an acidulation of 1.81 lb of sulfuric acid per lb of rock  $P_2O_5$ . This corresponds to the acidulation used commercially to prepare superphosphate. With this process, the solvent was mixed with the acidulated rock slurry and then the phases were separated. There was never a clear aqueous layer present during the extraction when acids of concentration higher than 60 per cent were used. The other procedure that was studied used an initial acidulation of 2.50 lb sulfuric acid per lb of rock  $P_2O_5$ . This is the acidulation commonly used to produce wet process phosphoric acid. The solvent was mixed with the over-acidulated rock and then the phases were separated. When this process was used, the aqueous phase separated into two layers, a slurry of acidulated rock on the bottom and a clear liquid above. After the solvent was removed, sufficient additional phosphate rock was added to the aqueous phase to reduce the over-all acidulation to 1.81 lb sulfuric acid per lb of  $P_2O_5$ . Superphosphate was obtained as the final product. The maximum

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<sup>1</sup>Doctoral thesis number 1660, submitted May 20, 1955. Chairman of Committee, G.L. Bridger, Department of Chemical Engineering.

<sup>2</sup>B.S., Iowa State College, Ames.

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uranium recovery obtained by either method was about 50 per cent of that present in the acidulated rock.

A considerable amount of solvent was occluded by the freshly acidulated rock. The samples prepared in the laboratory were filtered and washed with kerosene but even with vacuum filtration some organic matter was still held by the fresh superphosphate. It was concluded that a drying operation would be necessary to completely remove the organic materials. Kerosene has too high a boiling range to be removed by drying. A lower boiling material such as n-heptane would have to be used. The quick-cure process for production of superphosphate uses a drying operation to cure the material. A similar process could be used to simultaneously cure the superphosphate and remove organic materials.

The uranium recovery seemed to be limited mainly by two factors. One of these was the extent of apatite lattice destruction by the sulfuric acid. This was measured by  $P_2O_5$  conversion. Only uranium freed from the apatite lattice can be recovered by solvent extraction. The other limiting factor was the possible formation of  $UF_4$  during the acidulation of the rock. Uranium tetrafluoride is insoluble in octyl pyrophosphoric acid. The use of oxidizing agents, which may have formed  $U^{+6}$  thereby preventing the formation of  $UF_4$ , during the acidulation had a beneficial effect on uranium recovery.

Although the maximum uranium recovery obtained was only half of that present in the acidulated rock, it still represents a domestic source of approximately 500 tons of uranium annually. A raw material cost study indicated that an acidulation-extraction process may be economically feasible if the octyl pyrophosphoric acid and diluent could be recovered from the superphosphate. It was concluded that the process warranted further study to determine if uranium recovery can be increased.

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## COMPRESSIBILITIES OF SOME RARE EARTH NITRATES AND CHLORIDES IN AQUEOUS SOLUTION<sup>1</sup>

Gordon Atkinson<sup>2</sup>

Department of Chemistry

An apparatus for the precise determination of the adiabatic compressibilities of electrolytic solutions was constructed. This apparatus was a modification of the original ultrasonic interferometer of G. W. Pierce. The interferometer was of the variable path type, and was designed to operate at two megacycles. It was calibrated by numerous measurements on the compressibility of water at 25°C.

The actual quantity measured in the apparatus was the velocity of sound in the solution being studied. This was used to calculate the adiabatic compressibility of Newton's equation:

$$\beta_a = \frac{1}{v^2 d}$$

where  $\beta_a$  is the adiabatic compressibility,  $v$  is the velocity of sound, and  $d$  is the density of the solution.

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<sup>1</sup>Doctoral thesis number 1811, submitted June 4, 1956.

Chairman of Committee, Frank H. Spedding, Department of Chemistry.

<sup>2</sup>B.S., Lehigh University, Bethlehem, Pennsylvania.

Research Assistant, Institute for Atomic Research.

The compressibilities of lanthanum, neodymium, erbium and ytterbium nitrates and chlorides were measured at 25.0°C over the concentration range 0 to 0.4 molal. It was found that the compressibility data for a given salt could be represented by the equation:

$$\beta = \beta_0 + A_m + Bm^{3/2}$$

In this equation  $\beta_0$  is the compressibility of the pure solvent and  $A$  and  $B$  are characteristics of the salt. The apparent molal compressibilities were then calculated from the adiabatic quantities. For all the salts measured they followed the equation:

$$\Phi_k = \Phi_k^0 + B'm^{1/2}$$

In this equation  $\Phi_k^0$  and  $B'$  are characteristic of the salt. Equations for the partial molal quantities were then derived from the apparent molal equations.

The slopes of the partial molal compressibility lines differed from the predicted Debye-Hückel slope by at least 150 per cent. This deviation and the individuality of the slopes demonstrate clearly the inadequacy of the theory with respect to the volume quantities. It was found that the use of the measured compressibilities in the calculation of the theoretical Debye-Hückel partial molal volumes improved theory-experiment agreement by 15 per cent, but still left a large discrepancy at the high concentration end.

A critique of recent hydration number calculations was given together with suggestions for improving the calculations.

A tentative explanation of the apparent anomalies in the partial molal volumes and compressibilities of rare earth solutions was advanced. These and other measurements suggest that there are two primary hydration numbers for the rare earth ions in solution. Shifts from one hydration number to another cause the properties to deviate from a simple straight line dependence on crystal ionic radius. Suggestions for further experimental and theoretical work on the volume effects of the rare earths were made.

#### PHOTO-REDUCTION OF KETONES BY HYDROGEN DONORS IN SOLUTION<sup>1</sup>

William Perrin Baker, Jr.<sup>2</sup>

Department of Chemistry

Several ketones were photo-reduced in the presence of a hydrogen-donating solvent. The light source was an 800 watt short arc mercury lamp. The light was rendered approximately parallel by a quartz lens, transmitted through a filtering system to the cell, and then focused by a second quartz lens onto a thermopile which was connected to a potentiometer. The apparatus was calibrated with the uranyl oxalate actinometer.

Two different filtering systems were employed. One system transmitted the majority of light at 3660 Å, and the other transmitted the majority at

<sup>1</sup>Doctoral thesis number 1722, submitted September 24, 1955.

Chairman of Committee, G.S. Hammond, Department of Chemistry

<sup>2</sup>B.S., Haverford College, Haverford, Pennsylvania. M.S., University of Wisconsin, Madison. Graduate Assistant, Industrial Science Research Institute.

3130 Å. Both benzophenone and *p,p'*-dimethoxybenzophenone had higher quantum yields at the longer wavelengths. No other ketones were photo-reduced at both wavelengths.

When toluene was employed as the solvent, dilution of the toluene with benzene decreased the quantum yield of the benzophenone photo-reduction. The quantum yield of the photo-reduction of benzophenone was higher in diphenylmethane than toluene. Only a small variation of quantum yield was observed with variation of the ketone concentration. The quantum yields were independent of light intensity. Benzophenone was found to photo-reduce quantitatively to benzopinacol and diphenylbenzyl carbinol. The other ketones were assumed to do likewise, and the various pinacols were determined by lead tetraacetate titration.

On the basis of the experimental results reported in the thesis and the previously reported spectroscopic studies of others, certain hypotheses have been developed. The most pertinent observations from spectroscopy which have been used are that there is rapid degradation of excited states by thermal means, and that there is a triplet state of ketones which lies slightly lower than the  $E_1$  singlet. The most significant experimental observations are:

1. The quantum yield of the photo-reduction decreased as light of shorter wavelength was used, but under all conditions it was larger than can be reasonably accounted for on the basis of direct excitation to the triplet state alone. At 3660 Å the quantum yields in toluene varied from 0.35 with benzophenone to 0.16 with acetophenone.
2. The inverse of quantum yield varied with the inverse of the toluene concentration in benzene-toluene mixtures.
3. The quantum yield was higher in diphenylmethane than in toluene.
4. The product ratio did not vary with a substitution of benzophenone.
5. Less cross coupling occurred with acetophenone than with benzophenone and derivatives of benzophenone.

The hypotheses advanced to account for these facts are as follows:

1. The more, or only, photochemically active excited species under the experimental conditions is the triplet state.
  2. The conversion of the  $V_1$  excited state to the  $E_1$  state is not quantitative in solution.
  3. In the hydrogen transfer step the hydrogen is bound to the carbonyl oxygen to an extent such that the resonance energy of the forming solvent radical is exhibited. The transition state is rather loose.
  4. The transition states of the radical coupling reactions studied are loose, but they are not so loose that long range steric forces are negligible.
  5. The three-electron bond to a hydroxy group may contribute resonance energy of a magnitude similar to an aromatic nucleus.
  6. The cage effect was negligible in the systems studied.
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MICROBIOLOGICAL AND FUNCTIONAL CHANGES IN DRIED EGG ALBUMEN STORED AT ELEVATED TEMPERATURES<sup>1</sup>George J. Banwart<sup>2</sup>

Department of Bacteriology and the Committee on Food Technology

This investigation was undertaken to study methods of enumerating and procedures for eliminating organisms of the genus Salmonella in dried albumen; also an attempt was made to determine the effect of high temperature storage upon the functional properties of dried albumen.

Nutrient broth was observed to support the growth of Salmonella better than any of the enrichment media tested. When comparisons were made between the enrichment broths, Selenite-F or tetrathionate allowed better growth than did Ruys' medium. Of the selective agars utilized, brilliant green was the least inhibitory to the growth of Salmonella.

Adjustment of egg white to an alkaline pH retarded the growth of Salmonella. The antibiotics chlortetracycline, oxytetracycline or streptomycin retarded the growth of Salmonella, although the presence of egg white masked the effects of these bacterial inhibitors.

Egg white inoculated with S. pullorum, S. oranienburg, or S. senftenberg was dried, adjusted to 1.5, 3, 6, or 12 per cent moisture and stored at 50°, 60°, or 70°C. As the temperature of storage was increased from 50° to 70°C, the death rate of Salmonella was increased proportionally. In general, as the moisture content of the albumen was increased, the death rate of Salmonella was increased. There was no apparent difference in the rate of death of Salmonella in albumen containing either 1.5 or 3 per cent moisture.

Under the conditions of this study, S. oranienburg was more resistant to loss of viability during storage of dried albumen than were either S. senftenberg or S. pullorum. These species of Salmonella survived storage better in pan dried albumens than they did in spray dried albumens.

Volume of resultant angel cakes was more affected by storage of dried albumen than were either solubility or beating rate of the albumens; however, it was possible to store dried albumen containing 1.5 or 2 per cent moisture at 60° or 70°C in order to eliminate large loads of Salmonella without significantly impairing angel cake-making properties of the reconstituted albumen. High counts of Salmonella were eliminated in dried albumen containing 1.5, 3, or 6 per cent moisture and stored at 50°, 60°, or 70°C without noticeably affecting either solubility of the dried albumen or beating rate of the reconstituted product.

<sup>1</sup>Doctoral thesis number 1721, submitted September 19, 1955.

Chairman of Committee, John C. Ayres, Committee on Food Technology.

<sup>2</sup>B.S., Iowa State College, Ames. Graduate Assistant.

ABSORPTION AND TRANSLOCATION OF 2,4-DICHLOROPHENOXYACETIC ACID AND OF RADIOACTIVE PHOSPHORUS<sup>1</sup>George Edgar Barrier<sup>2</sup>

Department of Botany

The development of systemic herbicides has served to re-emphasize the importance of absorption and translocation in applied plant physiology. Absorption and translocation of the systemic herbicides, of which 2,4-D is the prototype, are necessary before these compounds can affect the growth of untreated plant parts. Both absorption and translocation have been studied in detail, but the mechanisms involved are still obscure. The absorption and translocation of 2,4-D and P<sup>32</sup> were investigated and compared in the experiments reported here.

The experimental plant materials were soybeans and detached sugar beet leaf blades. Soybeans were generally treated with 2,4-D by dipping two-thirds of one unifoliate of each plant in a solution containing 750 ppm of the sodium monohydrate and 0.1 per cent of a wetting agent, Triton B-1956. One microcurie of P<sup>32</sup> in 10  $\mu$ l of a mildly acid phosphate solution was applied to one unifoliate leaf of each soybean plant. Excised beet leaf blades were treated by spreading a solution of radioactive phosphorus and Triton X-100, a wetting agent, over them with a soft brush. Subsequent growth responses of soybeans were used to measure the quantity of 2,4-D in the plants. The P<sup>32</sup> contained in soybean plants was analyzed by counting briquets pressed from the dried material with a geiger counter. The excess P<sup>32</sup> was washed from the beet leaves and the quantity and distribution within the blades observed in radioautographs.

Movement of 2,4-D from soybean leaves was found to lag behind penetration of the herbicide by two hours or more. This difference in rate constituted the basis for studies of absorption and translocation as independent processes.

Radioactive phosphorus was distributed throughout soybeans one week after application, with much of the translocated P<sup>32</sup> in portions which had developed since treatment. Only 16 per cent of the P<sup>32</sup> applied was absorbed by treated leaves and only about one-third of this was translocated from them.

None of five wetting agents tested caused a statistically significant increase in the absorption of labeled phosphate, but two of them, Dreft and B-1956, significantly decreased absorption in the two experiments where 20  $\mu$ l of total solution was used. These findings are in sharp contrast to the results of other workers who found surface active agents to increase the absorption of 2,4-D.

The addition of 5 per cent sucrose to 2,4-D solutions applied to carbohydrates depleted soybean leaves had little influence on the absorption of this herbicide. In contrast, plants placed in the dark for 24 hours before treatment absorbed less P<sup>32</sup> than lighted plants. Whether the plants were in the light or dark after treatment had little effect on the absorption of P<sup>32</sup>. The effect is assumed to have been due to electrical charge differences rather than to carbohydrate depletion.

The absorption of 2,4-D by soybean leaves exhibited a temperature coefficient of approximately 2, while the rate of absorption of P<sup>32</sup> at 15°C differed little from the rate at 30°C. Absorption of 2,4-D by soybean roots in cultural solutions was found to have a Q<sub>10</sub> near 1. The results of these and the other experiments are discussed in terms of possible mechanisms.

<sup>1</sup>Doctoral thesis no. 1778, submitted March 12, 1956. Chairman of Committee, W.E. Loomis, Department of Botany.

<sup>2</sup>B.S., Berea College, Berea, Kentucky. M.S., North Carolina State College, Raleigh. Graduate Assistant, Agricultural Experiment Station.

The amounts of carbohydrates in soybean leaves influenced the rates of translocation of 2,4-D and  $P^{32}$  from them. Sucrose applied above, or mixed with the 2,4-D or  $P^{32}$ , increased translocation from carbohydrate depleted leaves. When sucrose was applied below the  $P^{32}$ , translocation from treated leaves was not affected.

When 2,4-D was applied in a nonphytotoxic oil it was shown to move from carbohydrate depleted leaves, while little moved from similar leaves treated with 2,4-D, using water as the carrier. Mechanical movement rather than translocation in the phloem was apparently responsible.

Temperature was found to be the limiting factor in the translocation of both 2,4-D and  $P^{32}$  in the range of 15 to 30°C. The results of these and the previous experiments with translocation are discussed in terms of the nature of the mechanism involved. The temperature coefficients of translocation varied from 1.63 to 2.37, indicating that the process is limited at some point by chemical action.

Radioautographs demonstrated that  $P^{32}$  was accumulated in the veins of excised beet leaf blades, even though movement from the leaves was absent. The level of carbohydrates in the leaves was found to influence the quantity of  $P^{32}$  loaded into the veins. These results are evidence for a loading operation dependent upon respiratory energy as the first step in translocation.

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## THERMAL EXPANSION OF RARE EARTH METALS<sup>1</sup>

Fred Barson<sup>2</sup>

Department of Physics

A high temperature dilatometric investigation of the rare earth metals was undertaken as part of a broad program of study of these elements, the ultimate goal being better understanding of metals in general. The more immediate goal, in addition to determining the coefficients of expansion quantitatively, was to detect evidence of any crystalline transformations which may occur and particularly to cast some light on certain high temperature transitions already discovered in several of these metals. The rare earth metals included in this investigation were lanthanum, cerium, praseodymium, neodymium, terbium, gadolinium, dysprosium, erbium, and ytterbium.

In view of the highly reactive nature of these elements at high temperatures and their relatively small thermal expansion, it was necessary to design and build a somewhat specialized dilatometer. The device employed consisted essentially of a quartz-tube and dial-indicator dilatometer in which an optical interferometer replaced the dial-indicator gauge. This increased the sensitivity of the instrument and made possible automatic recording of the results by means of a photomultiplier tube which detected motion of the interference fringes. Provision was also made for controlling and recording the sample temperature automatically and for placing an inert atmosphere about the sample during the course of the run. It was estimated that this apparatus was capable of determining the coefficient of expansion to about  $\pm 0.2 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$ , some 2 or 3 per cent of the value for a typical rare earth metal.

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<sup>1</sup>Doctoral thesis number 1806, submitted June 1, 1956.

Chairman of Department, Frank H. Spedding, Department of Physics.

<sup>2</sup>B.S., Iowa State College, Ames. M.S., *ibid*.

Graduate Assistant, Institute for Atomic Research.



Room temperature values of the coefficients of expansion, except in the case of ytterbium, were found to range from  $4.2 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$  for praseodymium to  $9.5 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$  for dysprosium. For ytterbium, a metal which assumes a divalent chemical form in compounds and generally has properties differing from most other members of the rare earth series, a room temperature coefficient of  $25 \times 10^{-6} \text{ }^{\circ}\text{C}^{-1}$  was observed.

An indication of the hexagonal to face-centered cubic transformation in lanthanum appeared as a volume change, with hysteresis, between about  $200^{\circ}\text{C}$  and  $320^{\circ}\text{C}$ . The higher temperature face-centered cubic modification was formed with an accompanying decrease in volume of some 0.3 per cent.

It was found that in the lower melting metals an excessive amount of creep developed at high temperatures, due, it was thought, to a rapid increase in the number of lattice imperfections. This creep was so great that it was impossible to take usable data through the regions of the high temperature transitions of lanthanum and cerium. In the cases of praseodymium and neodymium, however, evidence of high temperature transitions could be observed. These appeared as very slight volume changes, the higher temperature form of both metals being about 0.1 per cent larger by volume than the modification below the transformation temperature. In praseodymium this anomaly occurred at  $790^{\circ}\text{C} - 793^{\circ}\text{C}$ , while in neodymium it took place at about  $867^{\circ}\text{C}$ .

Since the Curie points of gadolinium and terbium had been reported not far below room temperature, an attempt was made to include this region in the study of these two metals by cooling the furnace prior to the runs. It was found that both of these metals exhibited a negative coefficient of expansion over a range of temperatures near to their reported Curie points, gadolinium from  $-40^{\circ}\text{C}$  to  $+28^{\circ}\text{C}$ , and terbium from  $-100^{\circ}\text{C}$  to  $-40^{\circ}\text{C}$ .

Dysprosium displayed a slight hysteresis loop in its expansion between  $650^{\circ}\text{C}$  and  $900^{\circ}\text{C}$ . Ytterbium apparently underwent a transformation of some sort in the high temperature region; however, the very high volatility of this metal may have interfered with the operation of the instrument, and this conclusion must be labeled as somewhat tentative for the present.

Attempts to calculate the Grüneisen constant from measured physical properties, including the expansion coefficients, resulted in values which were extremely low as compared with other metals. A second calculation of the same constant from compressibility data gave results which were somewhat higher, but still lower than the anticipated values. Attempts to correlate the thermal expansion of the rare earth metals with their melting points met with similar failure, the expansion being in most cases much lower than would be expected from comparison with other metals.

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EFFECTS OF CHEMICALS ON COLOR AND DURABILITY OF  
IOWA DEVONIAN SHALE PRODUCTS<sup>1</sup>Maynard Paul Bauleke<sup>2</sup>

Department of Ceramic Engineering

The effects of additions of urea, monobasic ammonium phosphate, dibasic ammonium phosphate, sodium ammonium phosphate, ammonium nitrate and ammonium chloride on selected physical properties of a high carbonate content illitic shale, unfired and fired were studied. Conventional methods of procedure and testing were used wherever possible.

The clay mineral content of the devonian shale was identified by X-ray methods. Illite was the predominant clay mineral present, with some chlorite also present. The versenate method of determining, by direct titration, the amount of magnesium and calcium present was rapid, efficient and adaptable to routine control testing.

Optimum additions of ammonium phosphates, one-half to one per cent, reacted with scum-producing sulfates to reduce scum formation and produce a clean surface. Excessive additions produced a scummed surface caused by the surface deposition of the added soluble ammonium phosphate. Additions of urea, ammonium nitrate and ammonium chloride did not reduce the formation of scum. The latter two additions created more scum than without their presence. Additions that caused the shale to stiffen, monobasic ammonium phosphate, ammonium chloride and ammonium nitrate, increased the fired absorption of the test bars. This was attributed to the clay mineral-chemical addition reaction which flocked the clay micelles into loose porous masses. An open packing resulted, creating more pore voids. Dibasic ammonium phosphate, sodium ammonium phosphate and urea either deflocculated the shale or had little effect on the workability of the shale, and produced only small changes in the fired absorption.

The type of anion present in the ammonium salt controlled the thixotropic or dilatant nature of the shale slip. The presence of chloride or nitrate ions created thixotropic conditions, while the phosphate ion created dilatant conditions.

The presence of ammonium chloride lowered the temperature at which oxidation began. All the necessary constituents of a catalyst were present in the shale. The presence of the catalyst will cause the ammonia to oxidize to nitrous oxide and nitrogen dioxide. Nitrous oxide, an oxidizing agent, forms at the low temperatures. At the higher temperatures the formation of nitrogen dioxide is favored. Nitrogen dioxide maintains an equilibrium with nitric oxide that converts ordinary oxygen into activated oxygen. Activated oxygen is extremely reactive. All of the ammonium additions used shortened the length of time required for complete oxidation of the shale specimens.

One per cent additions of chemicals that decreased the workability of the shale required additional water of plasticity for proper forming. Transverse strength with such additions present will usually be decreased. No difference was noticed for the breaking strength of dry and moist fired shale bars except when a sodium salt was used. The combination of a sodium compound and low firing temperature did not appear desirable for a high carbonate content shale having a low amount of glass bond present. The presence of moisture deteriorated the bond.

Only the one per cent addition of ammonium chloride in a shale fired to

<sup>1</sup>Doctoral thesis number 1770, submitted March 6, 1956.

Chairman of Committee, C.M. Dodd, Department of Ceramic Engineering.

<sup>2</sup>B.S., University of Alabama, Tuscaloosa. M.S., University of Illinois, Urbana. Instructor.

cone 07 produced any real improvement in the frost resistance. All the other additions showed poor frost resistance when fired to cone 07. Firing the shale to cone 02 produced a bar that was frost resistant. Additions had no effect on the frost resistance at cone 02.

None of the ammonium additions reduced the hydration of free lime formed by firing the shale to cone 07. Firing to cone 02 reacted most of the free lime with the other shale constituents and held the hydration to a minimum. The best method of reducing lime damage is to finely grind the initial carbonate present, thoroughly disperse it throughout the shale and fire it to about 2000°F.

The effects that the additions of ammonium salts will have on the unfired and fired properties of a shale will vary from shale deposit to shale deposit. It is recommended that thorough physical tests be made of the effects produced by the additions before adopting them for commercial use.

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### EVALUATION OF VARIOUS PHYSICAL AND NUTRITIONAL FACTORS RELATED TO BLOAT<sup>1</sup>

Joseph Thomas Blake<sup>2</sup>

Department of Animal Husbandry

Bloat research was conducted on 3 types of bloat, namely: green forage, feed lot, and chronic. Preliminary experiments were also conducted to determine best procedures and techniques to employ in conducting bloat research. With each type of bloat various popular prophylactic and therapeutic measures were evaluated. Rumen fluid properties from bloated and nonbloated cattle were compared, and the effect of preventives on these rumen fluid properties was studied *in vivo* and *in vitro*. Analyses were made of bloat provocative dry rations and forage extracts to determine any possible relationship between dietary properties and rumen fluid properties in regard to bloat severity.

Preliminary experiments in regard to collection, preparation, and storage of rumen fluid samples indicated the following: accurate surface tension readings were possible without extensive sample refinement; pH values differed with collection route (oral versus fistulae); surface tension radically changed inversely with sample temperature; only minor changes in surface tension occurred with short-time sample storage; extensive water dilution but only moderate saliva dilution were required to appreciably alter surface tension; surface tension and pH gradually decreased from 6 A.M. to 9 P.M. each day and surfactants decreased surface tension both *in vivo* and *in vitro*. The decreased surface tension occurring with additions of surfactants to rumen fluid does not assure that surface tension is etiological in bloat. However, if surface tension is etiological, and surfactants are preventive, it logically involves an abnormally high surface tension during actual bloat.

In animals bloated on pasture the rumen fluid surface tension, foam half-life, and viscosity were higher, specific gravity and pH were lower and foam was more extensive than with nonbloated animals in the same field. A sodium alkyl aryl sulfonate type detergent administered at a prophylactic level decreased incidence and severity of alfalfa pasture bloat and altered measured rumen fluid properties in the direction of nonbloated animals. Little distinct correlation between weather and bloat occurrence was observed.

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<sup>1</sup>Doctoral thesis number 1747, submitted December 8, 1955.

Chairman of Committee, N.L. Jacobson, Department of Animal Husbandry.

<sup>2</sup>B.S., Brigham Young University, Provo, Utah. M.S., Iowa State College, Ames. Graduate Assistant, Agricultural Experiment Station.



Bloat was produced from administration of extracts of alfalfa, Ladino clover, and grasses. Such bloat ranged from mild to severe and abdominal distention from minor to great. Fatal, nonreversible cases of bloat occasionally occurred. Crude saponin content was high in alfalfa, medium in Ladino clover, and low in brome and orchard grasses and birdsfoot trefoil. An aqueous emulsion of cholesterol precipitated the cholesterol precipitable saponins in alfalfa extract, but failed to reduce severity of forage extract bloat. As opposed to alfalfa pasture bloat, measured rumen fluid properties were not greatly different in forage extracted bloated as compared to nonbloated animals. Contrary to results obtained with alfalfa pasture bloat, a sodium alkyl aryl sulfonate type detergent, when administered with alfalfa extract, failed to reduce bloat severity.

Alfalfa extract, both whole (as extracted) and a supernatant fraction (liquid portion resulting from gravity separation of the whole extract) produced bloat in cattle, although pulp and chopped alfalfa did not. Fresh alfalfa extract was more bloat-provocative than stored extract (storage time ranged from 1 to 60 days). Addition of dextrose to forage extracts increased bloat incidence and severity. Dextrose in water was fatal when administered in large quantities at high concentrations.

Cyanide was found in both Ladino clover and trefoil extracts. However, the concentration in trefoil extract was much the higher. Birdsfoot trefoil extract was toxic in very small quantities, and also fatal unless antidote was employed. The green trefoil plant, however, produced no clinical symptoms of toxicity when introduced into the rumen of a steer through a fistula.

No experimental feed-lot ration (formulated specifically to produce bloat) successfully produced bloat at will in every animal employed. With several of the experimental rations some cattle were continually bloated and others never bloated. Bloat occurrence was not greatly related to extent of feed consumption. Alterations of a ration, which was producing bloat at the time, consisted of replacing dehydrated alfalfa with either dehydrated Ladino clover or dehydrated cereal grasses. Bloat incidence and severity were essentially unaffected by these changes. Moreover, additional dietary sources of basic ions, ammonia, or sulfur failed to influence bloat occurrence. In bloated animals the rumen fluid surface tension, viscosity, foam and pH were increased and specific gravity was decreased as compared to nonbloated animals on the same feed-lot ration.

Methyl silicone type defoaming agents were only slightly, if at all, effective against feed-lot type bloat at dosage levels up to 5 times recommended levels. No prophylactic or therapeutic measures employed were successful in permanently reducing or curing chronic bloat. Such measures included antiferments, antibiotics, surfactants, antifrothing agents, hydrogen-ion alterants, cholesterol and ration composition modifications.

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ESTIMATION OF SURFACE RUNOFF VOLUMES FROM  
AGRICULTURAL WATERSHEDS BY INFILTRATION THEORY<sup>1</sup>Donald L. Brakensiek<sup>2</sup>

Departments of Agricultural Engineering and of Statistics

The estimation of surface runoff volumes by infiltration theory was investigated with respect to western Iowa agricultural watersheds. Raw data for this study were infiltrometer tests, obtained during the Little Sioux Flood Control Survey, and antecedent and storm rainfall records for Sioux City, Iowa. The records covered the months May-September inclusive for the years 1907-1953 inclusive. Storms considered were limited to those classed as excessive by the U.S. Weather Bureau.

A method was developed for converting the differences between rates of rainfall and runoff from an infiltrometer test to infiltration capacities. The magnitude of the required corrections, namely the corrections for storage, were found to be small. Methods for fitting the infiltration capacity equation to a time sequence of infiltration capacities were investigated. The infiltration capacity equation generally accepted in the literature is represented by a curve commencing at an initial infiltration rate  $y(0)$  and gradually decreasing to a final infiltration rate  $y(\infty)$ . The (exponential) rate of decrease of the curve is measured by a third parameter  $k$ . In the case of "dry runs" the method of "internal moments" gave estimates for the parameters  $y(\infty)$ ,  $y(0)$  and  $k$  which compared well with the least square estimates. However, for "wet runs" a "modified method" had to be utilized. It was shown that the appropriate errors, the "between replicate" errors, i.e., discrepancies encountered from test to test, were much larger than the "within test" errors and hence a refined method of fitting aiming at a reduction of the latter errors was not warranted. Thus, because of its simplicity, the modified method was utilized for all tests. For the case of tests corresponding to a large  $k$  value it was shown that the "modified method" was related to the least square procedure.

Future infiltrometer tests should be designed so that runoff could be measured continuously and the duration of a run should be shortened. Under such a design more information would be obtained for the initial portion of a wet run test. The loss of information would be in the range of the curve that is of little use in a fitting procedure. As equidistant data for any length of interval could be obtained, the method of internal moments could be utilized for all runs. It would seem that the storage corrections might be neglected without serious error.

The models relating the parameters of the infiltration capacity equation, within a soil-crop complex, to antecedent rainfall via the API, (here called  $I'$ ), gave reasonable results. However, much more study is required on the use of the API, i.e., the functional form and the value of the recession coefficient,  $q$ . With this in mind future tests should be supplemented with more complete rainfall records of the particular site. Also initial soil moisture contents should be determined for each run. A series of tests should be conducted at each site over a period of several months so as to allow any seasonal effect to manifest itself. Such a collection of data would not only allow an evaluation of the recession coefficient,  $q$ , but also the rate of recovery of the infiltration capacity between storms.

Estimation of surface runoff volumes by the infiltration theory developed in

<sup>1</sup>Doctoral thesis number 1750, submitted December 8, 1955.

Chairmen of Committee, H. O. Hartley, Department of Statistics, and Richard K. Frevert, Department of Agricultural Engineering.

<sup>2</sup>B.S., University of Illinois, Urbana. M.S., *ibid*.

Graduate Assistant, Agricultural Experiment Station.

this study was made for a number of watersheds and was found to give reasonable results. Except for the watershed TDD the estimated runoffs were generally within  $\pm 20$  per cent of the measured runoffs. However, more information is needed on the correction to be made for depressional storage and vegetative interception. Considering the small amount of field data from which the infiltration characteristics were derived, the results of this study indicate that further field studies would be warranted for collecting infiltration data for Iowa agricultural watersheds. Compilation of such data would allow a rational estimation of surface runoff volumes on an individual storm basis or on an annual yield basis.

The consequence of using wet run infiltrometer data for estimating design runoff volumes was investigated. Antecedent precipitation indexes for naturally occurring storms were compared with those corresponding to wet run infiltrometer tests. The Sioux City, Iowa, data was utilized for this comparison. The Negative Binomial distribution was shown to fit the empirical frequency distribution. Probability statements obtained from the fitted distribution showed that the wet runs simulated an extreme design condition with respect to the infiltration capacity curve. The API's corresponding to the wet run infiltrometer tests for grass, small grain, and corn had a probability of occurrence of only once in 30 seasons,<sup>1</sup> 81 seasons, and 224 seasons, respectively. Considering a 3-year rotation of corn, oats, and clover, the probabilities of occurrence for the corresponding infiltration capacity curves would be only once in 90 seasons, 243 seasons, and 672 seasons. It was shown that there was a correlation between the total rainfall amount and the API associated with it. More study is needed to investigate the concurrence of an excessive rain storm and a large API.

Applications of the derived infiltration capacity curves and the developed procedure was made to the compiled Sioux City, Iowa, excessive rain storms. Estimates of excess rainfall were obtained for a Marshall silt loam - corn complex and the Negative Binomial distribution was fitted to the empirical frequency distribution. Utilizing the fitted distribution, probability statements were also made for certain excess rainfall depths. It was found that an excess rainfall depth of 2.00 inches or more would be expected to occur only once in 50 seasons. Also a depth of 1.30 inches or more would be expected to occur only once in 10.8 seasons. It would seem that the rationale for designing level terraces in western Iowa should be re-evaluated.

Only estimation of volume of surface runoff was investigated in this study. Hence before the present results can be utilized in design problems for a particular watershed the surface runoff hydrograph must of course be studied to take account of such factors as topographical features of the watershed.

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<sup>1</sup>Season refers to the calendar period May-September inclusive.

PROTEOLYSIS BY *LACTOBACILLUS CASEI*<sup>1</sup>Erling Brandsaeter<sup>2</sup>

Department of Dairy Industry

*Lactobacillus casei* is an organism commonly found in cheese. It is known to possess proteolytic enzymes, and it probably is responsible for part of the protein degradation which takes place in most hard rennet cheeses. The exact role played by *L. casei* in the cheese ripening process is not known although this problem has been studied by several workers.

In the present study an attempt has been made to characterize some of the proteolytic enzymes of *L. casei*. Some of the information obtained may help explain the role this organism plays in the protein degradation in cheese.

Four different strains of *L. casei* all showed proteolytic activity when grown in milk. There was, however, considerable difference in proteolytic activity by the different strains; this was most apparent during the early stages of the incubation period. There were indications that the differences were due to variations in growth rate rather than to variations in enzyme production by the different strains. Maximum proteolytic activity when the organism was grown in milk at 36°C occurred between pH 5.5 and 6.5. Optimum temperature for proteolysis depended somewhat on the time of incubation. When tests were run for 96 hours, maximum protein degradation occurred at 32°C, the lowest temperature used in this experiment. Addition of chalk to the milk caused a considerable increase in proteolysis by *L. casei* when incubated for 4 days or more.

For preparation of cell-free extracts of *L. casei* the organism was grown in a modified Briggs medium at 36°C for approximately 24 hours. The cells were harvested in a Sharples Supercentrifuge (30,000 rpm), washed twice in 0.03 M phosphate buffer at pH 7.0, and finally dispersed in the same buffer at a ratio of wet cells to buffer of approximately 1:2. The cells were disrupted by sonic vibration in the chilled cup of a Raytheon 9 kilocycle magnetostriction oscillator. The cell debris was centrifuged out and washed once with phosphate buffer (0.03 M, pH 7.0). The cells obtained from growth in 6 liters of the medium yielded 120 to 140 ml of cell-free extract.

The proteinase activity of the cell-free extract was tested on a 2 per cent casein suspension. Maximum proteinase activity, as measured by increase in nitrogen soluble in 2 per cent trichloroacetic acid, occurred at progressively lower pH levels as the temperature was increased from 10 to 50°C. At 40 and 50°C the maximum activity occurred near pH 6.0. and at 30°C between pH 6.5 and 7.0. Maximum proteolytic activity at pH 6.0 occurred at approximately 50°C.

The rate of increase in noncasein and amino nitrogen was maximum at pH 5.5 when a temperature of 45°C was employed. Under the same conditions, the maximum rate of increase in nonprotein nitrogen occurred at a slightly lower pH level, indicating the possible presence of two proteinase systems.

Maximum heat stability of the proteinase activity occurred at pH 5.0 to 5.5. The enzymes retained 60 per cent of its activity after heating at pH 5.0 and 61.7°C for 10 minutes.

The cell-free extract of *L. casei* hydrolyzed a series of di- and tripeptides. The maximum rate of hydrolysis of four different peptides at pH 7.0 occurred between 45 and 50°C. Generally the glycyI-peptides were hydrolyzed at a maximum rate between pH 7.5 and 8.0, whereas for the alanyl- and leucyl-peptides the corresponding pH values were approximately 7.0 and 7.5 at 45°C.

<sup>1</sup>Doctoral thesis number 1712, submitted August 15, 1955.

Chairman of Committee, F.E. Nelson, Department of Dairy Industry.

<sup>2</sup>B.S., Agricultural College of Norway. M.S., Iowa State College, Ames.



Glycylglycine and diglycylglycine were hydrolyzed at a very low rate. DL-alanyl-DL-alanine was hydrolyzed rapidly over a wide pH range. The rate of hydrolysis of DL-alanylglycylglycine, which was maximum at pH 7.0 or slightly below, decreased rapidly as the reaction was raised above pH 7.0.

The effect of metallic ions on the enzymatic hydrolysis of peptides was tested. Nickel slightly activated the hydrolysis of glycyl-DL-alanine at pH 6.0 and 8.0, and strongly inhibited the hydrolysis of DL-alanylglycine, DL-leucylglycine and DL-alanylglycylglycine at pH 7.0, but had little effect on the hydrolysis of five other peptides tested. Copper and manganese were inhibitory or had no effect on the peptidase activity by cell-free extract of *L. casei*. Magnesium inhibited the hydrolysis of glycylglycine and diglycylglycine, but otherwise had little effect. Zinc activated the hydrolysis of most peptides at pH 7.5 to 8.5, but had little effect at lower pH levels. Cobalt was found to have the greatest effect on the enzymatic hydrolysis of peptides. It strongly activated the hydrolysis of most peptides at pH 5.5 to 6.0, but strongly inhibited the hydrolysis of alanyl- and leucyl-peptides between pH 7.0 and 8.5. The hydrolysis of glycylglycine was strongly activated by cobalt at both pH 5.5 and 7.7. The remaining glycyl-peptides tested were less affected by cobalt at higher pH levels. The hydrolysis of DL-alanyl-DL-alanine was not affected by cobalt.

The peptidase activities had maximum heat stability at pH 6.0. There were some indications that the enzyme activities in the presence of cobalt at pH 5.5 were less stable than the activities in the absence of cobalt, which may indicate that two enzyme systems were present.

Attempted separation and purification of the cell-free extract of *L. casei* by fractional precipitation and selective adsorption and elution, revealed that possibly two proteinase systems were present. This was confirmed by experiments with zone electrophoresis on starch. The adsorption studies indicated that two peptidase systems were present. Glycyl-DL-alanine and DL-alanylglycine probably were hydrolyzed by different enzymes, and possibly a third enzyme was responsible for the hydrolysis of glycylglycine at pH 7.7 in the presence of cobalt. One enzyme possible was responsible for the hydrolysis of several peptides at pH 5.5 in the presence of cobalt. The enzyme activity at pH 5.5 in the presence of cobalt was not separated from the activity of DL-alanylglycine at pH 7.0. In experiments with zone electrophoresis on starch, one fraction was obtained which was active on glycyl-DL-alanine, but not on DL-alanylglycine; another fraction hydrolyzed glycyl-L-tyrosine at pH 5.7, but was not activated by cobalt. However, the majority of the peptidase activity was obtained in one fraction. Possibly the conditions under which the experiments were carried out were not such as to give maximum resolution of the enzyme activities.

Some of the peptidases of *L. casei* were strongly activated by cobalt at pH 5.5, which is comparable to the pH in ripening Cheddar cheese. However, addition of cobalt to Cheddar cheese had little effect on the quality or the protein degradation in the cheese. A possible improvement in flavor after 4 months was observed in the cheeses where cobalt was added in a concentration of 0.023 per cent or higher, calculated as cobalt sulfate in per cent of fresh cheese.

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INTERRELATIONS OF SOIL AND CROP MANAGEMENT PRACTICES  
IN GRAIN SORGHUM PRODUCTION<sup>1</sup>Paul Lawson Brown<sup>2</sup>

Department of Agronomy

The influence of plant population, row spacing, and available soil moisture at planting time on grain sorghum production was studied at Hays, Kansas, on Tripp silt loam, a well-drained alluvial soil, in 1954 and 1955. Plant populations varying from 15,000 to 120,000 plants per acre in 10-, 20-, and 40-inch rows were used. Three levels of available soil moisture were established prior to planting the crop by applying water to wet the soil to field capacity to depths of 3, 5, and 7 feet. The actual amounts of available soil moisture at planting time were, approximately, 6, 10 1/2, and 14 1/2 inches. No water, other than rainfall, was added after the crop was planted.

In 1954, the grain yields averaged 21.0, 35.6, and 48.2 bushels per acre for initial soil moisture depths of 3, 5, and 7 feet. In 1955, the grain yields averaged 1.7, 11.6, and 33.1 bushels per acre for the same initial soil moisture depths. In both years, seasonal rainfall was below normal. The lower yields in 1955 were believed to be the result of low rainfall during the critical heading period in August. August rainfall in 1955 was only 0.51 inch as compared to 2.66 inches in August, 1954.

Twenty-inch rows produced the highest yields in 1954 with 3 and 5 feet of initially moist soil. With a moisture depth of 7 feet, 10- and 20-inch rows produced the same yields and averaged 10 bushels per acre more grain than did 40-inch rows. The average yields for 10-, 20-, and 40-inch rows in 1954 were 35.0, 38.0, and 31.8 bushels per acre, respectively. In 1955, 40-inch rows produced the greatest yields at all three moisture levels. The average yields for 10-, 20-, and 40-inch rows were 11.8, 15.4, and 19.2 bushels per acre, respectively.

The optimum plant population varied with initial soil moisture depths in the two years. In 1954, 30,000 plants per acre produced the highest grain yields with 3 feet of moist soil although yield differences between populations in the 20- and 40-inch rows were not great. With 5 and 7 feet of moist soil, populations of 60,000 and 90,000 plants per acre, respectively, produced the greatest yields. In 1955, 15,000 plants per acre produced the highest grain yields with 3 feet of moist soil. With 5 and 7 feet of moist soil, populations of 30,000 and 30,000 to 60,000 plants per acre, respectively, produced the highest yields.

A fertilizer experiment was conducted in 1954 to determine the effect of nitrogen and phosphate on grain sorghum yields at initial soil moisture depths of 3 and 7 feet. At no time during the growing season was there any evidence of fertilizer response, and yields were not increased by the fertilizers.

The amount of water required to produce the first bushel of grain was estimated to be 7.8 acre-inches in 1954 and 11.0 acre-inches in 1955. The higher requirement in 1955 was attributed to lack of effective rainfall during the heading period in 1955.

The value of an acre-inch of stored subsoil moisture varied with the initial soil moisture depths in the two years. In 1954, an acre-inch of soil moisture was equal to 4.9 bushels of grain at the 5-foot moisture depth and 6.4 bushels of grain at the 7-foot moisture depth. In 1955, an acre-inch of stored subsoil moisture was equal to 2.9 bushels of grain at the 5-foot moisture depth and 9.6 bushels of grain at the 7-foot moisture depth.

<sup>1</sup>Doctoral thesis number 1792, submitted May 25, 1956.

Chairman of Committee, W.D. Shrader, Department of Agronomy.

<sup>2</sup>B.S., Kansas State College, Manhattan. M.S., *ibid*.

The crop used nearly all available water each year. In 1954, the crop used 12.00, 15.00, and 17.01 inches of water on the 3-, 5-, and 7-foot moisture plots. Water in the soil at planting time supplied 46, 57, and 62 per cent of the total amount of water used on the 3-, 5-, and 7-foot moisture plots, respectively. In 1955, the crop used 11.22, 14.68, and 16.89 inches of water on the 3-, 5-, and 7-foot moisture plots. Moisture in the soil at planting time supplied 52, 64, and 68 per cent of the total water used on the 3-, 5-, and 7-foot moisture plots.

The amount of water required to produce a pound of grain decreased as soil moisture depths increased. In 1954, 2596 pounds of water were required to produce a pound of grain on the 3-foot moisture plots. On the 5- and 7-foot moisture plots, 1898 and 1580 pounds of water, respectively, were required to produce a pound of grain. In 1955, the amount of water required to produce a pound of grain was considerably higher. On the 7-foot moisture plots, the requirement was 2469 pounds of water.

Root penetration was determined by the use of plaster of Paris soil moisture blocks. Soil moisture content remains relatively constant at depths below the surface as long as there are no roots present to absorb water. Soil moisture block resistance readings also remain relatively constant under these conditions. Thus, root penetration under low rainfall conditions can be detected by a change in resistance reading. In 1954, roots penetrated to a maximum depth of 78 inches. In 1955, roots penetrated to 90 inches.

Water absorption zones were also determined using the soil moisture blocks. A block resistance reading of 80,000 ohms is considered to be at or near the permanent wilting percentage of soil. As determined by moisture block resistance readings, the roots in 1954 absorbed water from the entire zone of root penetration until late in the growing season when certain soil depths dropped to the permanent wilting percentage moisture content. In 1955, the zone of water absorption was confined to a root zone of only 2-3 feet at any one time. In late July, the zone was near the soil surface and progressed downward with time. Once roots had entered a soil zone, the moisture content was reduced to the permanent wilting percentage in 2 to 3 weeks.

The results clearly indicate that with limited growing season rainfall, optimum plant populations and row spacings depend on the amount of available stored soil moisture at planting time. The depth to which a soil is wet is a measure of available soil moisture. With less than 3 feet of moist soil, a population of not more than 30,000 plants per acre is indicated. With 3 to 5 feet of moist soil, plant populations of 30,000 to 60,000 plants per acre is indicated. With 5 to 7 feet of moist soil, plant populations of 60,000 to 90,000 plants per acre are indicated. Narrow row spaces are indicated for deep moisture storage while wide spaced rows are indicated for limited moisture storage.

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CORN PRODUCTION SURFACES AND ECONOMIC FERTILIZER USE<sup>1</sup>William G. Brown<sup>2</sup>

Department of Economics and Sociology

A primary objective of this study was to estimate the relationship between inputs of fertilizer and corn yield. Then, from the basic yield predicting equations, the economic aspects of the production surface could be explored. To this end, three experiments were analyzed. These experiments were designed to allow estimation of the yield-fertilizer production surface. Nitrogen, phosphorus, and potassium were applied to corn on each experiment.

The Carrington soil experiment consisted of two randomized blocks of 60 nutrient combinations or a total of 120 observations. The five rates of N were 0, 40, 80, 160, and 240 lbs. Phosphorus applications were at the rate of 0, 40, 80, and 120 lbs of  $P_2O_5$ . Potassium treatments were 0, 40, and 80 lbs of  $K_2O$ . The Carrington soil experiment, as were the other two experiments, was completely factorial with every level of each nutrient being combined with every level of the other nutrients. A highly significant response to potassium was found in the Carrington soil experiment even though unfertilized plots averaged 98 bushels per acre. The production function selected for economic analysis was (31).

$$\hat{Y} = 99.223 + 0.3162K - 0.001813K^2 + 0.9190 \sqrt{N} - 0.04453N. \quad (31)$$

The same factorial design (five levels of N, four levels of P, and three levels of K) was used on the Moody soil experiments as for the Carrington experiment. Yield observations were more than doubled by some rates of nitrogen. Phosphorus had its greatest effect on yield through its complementary interaction with N. Potash did not appear to increase yields. The production function selected for the Moody soil experiment was equation (22).

$$\hat{Y} = 29.248 + 0.5340N - 0.001743N^2 - 0.0003549P^2 + 0.001069NP. \quad (22)$$

Corn yields responded to all three nutrients in the experiment on Haynie soil. Nitrogen response was greatest followed by lesser responses from  $P_2O_5$  and  $K_2O$ . Experimental rates for each nutrient were 0, 40, and 80 lbs. Improved estimation of the production surface might have resulted from higher rates of N and P and from heavier stand rates. The production function which seemed most appropriate for the Haynie soil data was (29).

$$\hat{Y} = 35.0587 + 0.7126N - 0.004352N^2 + 0.5255P \\ - 0.003103P^2 + 0.2546K - 0.001624K^2 - 0.002255PK. \quad (29)$$

Perspective drawings of the predicted yield surfaces for each experiment were presented along with individual response curves, isoquants, and isoclines. Isoclines are optimum "fertilizer mix" lines for given prices of fertilizer nutrients. For the Moody soil experiment, the optimum combinations of N and  $P_2O_5$  are given by (24) where  $\alpha$  represents the  $P_2O_5$ -N price ratio.

$$P = \frac{(0.001069 + 0.003486\alpha)N - 0.5340\alpha}{0.001069\alpha + 0.0007098}. \quad (24)$$

<sup>1</sup>Doctoral thesis number 1739, submitted December 2, 1955.

Chairman of Committee, Earl O. Heady, Department of Economics and

<sup>2</sup>B.S., Kansas State College, Manhattan. M.S., Iowa State College, Ames. Graduate Assistant, Agricultural Experiment Station.



Optimum rates and combinations of fertilizer for specified crop and nutrient prices were found for each experiment. Optimum inputs were found by setting the partial derivatives of  $\hat{Y}$  in the production function with respect to the nutrient equal to the nutrient-crop price ratio. For the Haynie soil experiment, (38), (39), and (40) give the optimum fertilizer inputs where corn is \$1.00 per bushel and N,  $P_2O_5$ , and  $K_2O$  are 15¢, 10¢, and 8¢ per lb, respectively.

$$\frac{\partial \hat{Y}}{\partial N} = 0.7126 - 0.008704N = \frac{0.15}{1.00} \quad (38)$$

$$\frac{\partial \hat{Y}}{\partial P} = 0.5255 - 0.006206P - 0.002255K = \frac{0.10}{1.00} \quad (39)$$

$$\frac{\partial \hat{Y}}{\partial K} = 0.2546 - 0.003248K - 0.002255P = \frac{0.08}{1.00} \quad (40)$$

Solving (38), (39), and (40), optimum inputs of 65 lbs of N, 66 lbs of  $P_2O_5$ , and 8 lbs of  $K_2O$  were indicated. Plugging these inputs into (29), a yield of 85 bushels was predicted. A net gain per acre of \$32.66 was estimated from the expenditure of \$16.84 per acre on fertilizer in this price situation.

Optimum inputs and predicted yields can be located by means of charts which are presented for use, where applicable, by extension personnel and farmers. Production functions are also used in a linear programming example to select the most profitable combination of enterprises where land, labor, and capital are limited. Of course, the production functions in this study apply only to specified soil types and fertility levels. Results may also vary from year to year due to changes in climatic and biological conditions. However, with the accumulation of experimental yield and soil test data, production functions which can take some of these variables into account may be possible.

#### PROFILE PROPERTIES AND SEQUENCE RELATIONSHIPS OF THE TRAER, BERWICK, AND MARION SERIES IN SOUTHEASTERN IOWA<sup>1</sup>

Charles C. Cain<sup>2</sup>

Department of Agronomy

An inverse relationship between loess thickness and profile development has been shown for a sequence of forested Planosol soils in southeastern Iowa. This agrees with a similar relationship reported for Brunizem and Wiesenboden soils by other workers.

Chemical and physical studies were made on selected profiles of the Traer, Berwick, and Marion series of this sequence. In addition a Marion profile from northeastern Missouri was also studied. Morphologically, these soils vary from the minimal Planosol profile of the Traer series to the very highly developed Planosol profile of the Marion series from northeastern Missouri. The loess thickness varied from approximately 300 inches at the Traer site in east central Iowa to 60 inches at the Marion site in northeastern Missouri.

<sup>1</sup>Doctoral thesis number 1793, submitted May 25, 1956.

Chairman of Committee, F. F. Riecken, Department of Agronomy

<sup>2</sup>B.S., Louisiana State University, Baton Rouge. M.S., Iowa State College, Ames.

A trend towards a distinct secondary zone of accumulation for total nitrogen and organic phosphorus in the B<sub>2</sub> horizons with increased profile development is shown for this loess-derived Planosol sequence. A sharp decrease in total nitrogen and organic phosphorus from the A<sub>1</sub> to the A<sub>2</sub> horizons is noted in each profile. This decrease became more abrupt with increased profile development. The per cent free iron tends to increase with increasing profile development but does not accumulate in the zone of highest clay content.

There is a trend towards decreasing pH with increasing profile development in this Planosol sequence. These soils are less acid than the associated Gray-Brown Podzolic soils and more strongly acid than the associated Wiesenboden soils. The ratio of exchangeable calcium to exchangeable magnesium in the B horizon of these soils decreases with increasing profile development except for the profile formed from thin loess.

Clay accumulation in the B horizon increases with decreasing loess thickness. Although appreciable differences were expected between profiles P-423 and P-421 the clay distribution curves are quite similar.

Other trends in physical properties accompanying increased profile development and decreased loess thickness are decreasing bulk density, decreasing aeration porosity, increasing capillary porosity, and increasing total porosity.

Profile development in this sequence of loess-derived Planosols is related to loess thickness and distance from loess source. These soils are considered to have been formed under the influence of similar vegetation and topography. Variations in temperature, rainfall, time of weathering, and particle size distribution of the loess seem to be of minor magnitude. However, the trends of these variations are such as to cause increased horizon differentiation in the sequence. In addition, the effect of these factors may be additive and their combined effect may account for the differences in profile development.

Another variable might be the hydrology of the sequence, as it seems likely that the Marion profile would be somewhat more waterlogged than the Traer profile due to the slowly permeable underlying paleosol. However, with the data obtained in this study it is not possible to evaluate the cause of the differences in the genesis of the sequence studied.

Profiles P-423 and P-421 should be included in the same soil series; namely, the Berwick series, and profile P-424 should be set apart in another series; namely, the Marion series. The minimal Planosol, profile P-422, which is developed from thick loess, should be set apart in the Traer series.

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## RESPONSE FUNCTIONS OF FARMERS IN USING FERTILIZER<sup>1</sup>

Luman Edward Cairns<sup>2</sup>

Department of Economics and Sociology

This study was concerned with the factors which influence farmers' decisions in the use of fertilizer. The central objective was to determine these factors and to estimate their importance. Attention was given primarily to economic factors although other factors affecting fertilizer use were recognized.

The data used in the investigation were obtained by personal interview

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<sup>1</sup>Doctoral thesis number 1761, submitted January 30, 1956. Chairman of Committee, Earl O. Heady, Department of Economics and Sociology.

<sup>2</sup>B.S., State College of Washington, Pullman.

Graduate Assistant, Agricultural Experiment Station.

from a sample of 184 farmers in three soil areas in northern Iowa. Multiple regression was used to estimate the relationships between the variables included in the study.

The amount of fertilizer used on owner-operated farms was related to the size of farm, capital investment and expenditure for fertilizer the previous year. On the other hand, the amount of fertilizer used on tenant-operated farms was related not only to size of farm, capital investment and fertilizer expenditure the previous year, as in the case of owner-operators, but also to the expected yield response from fertilizer. The marginal or additional increase in fertilizer use for a given increase in anticipated corn-yield response from fertilizer was greatest when capital investment, size of farm and use of fertilizer the previous year were greater. The marginal use of fertilizer was lower for higher anticipated corn-yield response from fertilizer applications.

On owner-operated farms the variables, capital investment, equity ratio and uncertainty of anticipated corn-yield response were positively related to the rate of nitrogen application on corn while equity ratio was related negatively. With respect to tenant-operated farms, the rate of nitrogen use was also positively related to capital investment and expected yield response from nitrogen, but was negatively related to the uncertainty of the expected yield response.

The data analyzed yield no relationships between fertilizer use and expected corn prices or other estimated parameters of the probability distributions of corn. This finding appears to be rather significant since it is inconsistent with the postulates of economic logic.

Owner-operators with more capital investment and a larger equity ratio considered themselves further from the "optimum" use of fertilizer. Similarly, tenant-operators with more capital investment considered themselves further from the "optimum" use of fertilizer. The variable fertilizer-use-experience was negatively related to the "difference" between present fertilizer use and the "optimum" use on tenant-operated farms; no relationship was observed between these variables in the case of owner-operators.

The proportion of an additional \$1000 an owner-operator would spend for fertilizer was positively related to capital investment and negatively related to equity ratio. On the other hand, the proportion of an additional \$1000 a tenant-operator would use for fertilizer was negatively related to fertilizer-use-experience, but also positively related to capital investment. Equity ratio was not related to an increase in expenditure for fertilizer in the case of tenant-operators, and fertilizer-use-experience was unrelated to increase in expenditures for fertilizer in the case of owner-operators.

Farmers' estimated yield responses from various levels of nitrogen were combined in regression equations by several groups: 1) corn grown first and second year after meadow, 2) owner-operators and tenant-operators, and 3) three soil areas. Estimates of yield response for corn grown the second year were significantly greater than for corn grown the first year after meadow. Tenant-operators tended to estimate higher corn-yield responses from nitrogen applications than did owner-operators. The extent of fertilizer use experience was negatively related to owner-operators expected variability of yield response, and positively related to expected yield response. The tenant-operators' variability of expected yield response was not found to be related to the years of fertilizer use experience.

The amount of nitrogen which farmers estimated they would use was inversely related to the nitrogen/corn price ratio. This relationship, which might be called a "subjective demand curve", slopes downward to the right in the conventional manner.

Of the several variables considered, capital investment, equity ratio and expectations of yield response appear to be more frequently associated with the decisions on the amount of fertilizer used. Other variables found to be related are farm size, quantity of fertilizer used the previous year, fertilizer

use experience and tenure status. It is particularly surprising that price expectations were not found to be related to fertilizer application in some regressions while the "subjective demand curve" showed a relationship between price and quantity. This inconsistency, along with the dubious nature of some of the functional relationships observed, suggest that prices, along with such variables as tenure status and uncertainty of yield response, need to be investigated further.

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### RECOVERY OF URANIUM FROM SLAG FROM THE ELECTRIC FURNACE PRODUCTION OF PHOSPHORUS<sup>1</sup>

Hobart Z. Cammack, Jr.<sup>2</sup>

Department of Chemical Engineering

When phosphate rock is reduced to elemental phosphorus with coke in the electric furnace process, the uranium in the phosphate rock virtually all goes into the by-product slag. It is estimated that approximately 300 tons of uranium is potentially recoverable per year from this use of phosphate rock.

Previous work at Battelle Memorial Laboratory, Mound Laboratory, and the Tennessee Valley Authority did not result in an economic process for the recovery of uranium from electric furnace slags. The present investigation included thermal reductions with alkaline earth metals, high temperature liquid-liquid extraction with molten extractants, solubilizing fusions, magnetic separations, and leaching with various solutions. As an adjunct to the high temperature liquid-liquid extraction studies, the solubility of uranium in antimony, bismuth, lead, silver, and tin were further studied, to corroborate and extend existing data.

Radioassay methods of analysis were developed for the raw furnace slags and residues from the various experimental treatments. A fraction of the slag residues were checked for uranium using a colorimetric procedure. All binary alloys resulting from the uranium solubility studies were analyzed with colorimetric procedures developed during the course of the investigation.

The results of the thermal reduction experiments do not indicate a concentration of uranium in either layer of mechanically partitioned slag residues. Bismuth, lead, and manganese appear to extract the most uranium from furnace slags by a single contact of the metal with the slag. In all high temperature extraction treatments, about 50 per cent of the uranium appeared amenable to extraction. The addition of calcium, magnesium, aluminum, and potassium to the melt with iron extractant appeared to improve the uranium extraction. Iron sulfides were found to extract approximately 45 per cent of the uranium from the slags by a single contact with the slags.

Contacting one portion of furnace slag with three successive portions of iron-calcium, bismuth, or iron sulfide extractant did not improve the total uranium extraction from the slag to above 50 percent. Contacting one portion of these extractants with several portions of furnace slag did not result in a marked increase of uranium concentration in the extractants. Because of the inability to build up a sizeable uranium concentration in an extractant, as shown in the study of uranium distribution between furnace slag and bismuth,

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<sup>1</sup>Doctoral thesis number 1716, submitted August 19, 1955. Chairman of Committee, G. L. Bridger, Department of Chemical Engineering.

<sup>2</sup>B.S., Iowa State College, Ames.

Graduate Assistant, Institute for Atomic Research.



the success of a proposed high temperature extraction process seems unlikely.

The only solubilizing fusion treatment which resulted in any appreciable elimination of uranium from the slag was the one with calcium chloride. The uranium was not found concentrated in the magnetic material in the slag. None of the leaching agents tried extracted an appreciable amount of uranium from the slag. Cost calculations based on data obtained indicate that none of the treatments studied would result in an economic recovery process.

The data obtained for the solubility of uranium in antimony agree fairly well with similar data reported by Massachusetts Institute of Technology. The data obtained for the solubility of uranium in bismuth agree with values interpolated from the established binary phase diagram, but lie below the values reported by Massachusetts Institute of Technology, and above values reported by Brookhaven National Laboratory. The data obtained for the solubility of uranium in lead agree with values reported by Massachusetts Institute of Technology, but lie below values interpolated from the established binary phase diagram. The data for the solubility of uranium in silver lie close to the reported solid solubility of uranium in silver, but lie well below the values reported by previous investigators. The data obtained for the solubility of uranium in tin agree with values reported by Massachusetts Institute of Technology, but lie below the values interpolated from the established binary phase diagram.

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### CALCIUM AND PHOSPHORUS STUDIES WITH GROWING-FINISHING SWINE<sup>1</sup>

Herbert L. Chapman, Jr.<sup>2</sup>

Department of Animal Husbandry

The calcium and phosphorus requirement of growing-finishing swine was investigated employing four replications of a partial seven by seven factorial design. Each replication consisted of twenty-five lots of three pigs each, for a total of 300 pigs. Dietary levels of calcium and phosphorus ranged from 0.2 through 0.8 and 0.2 through 0.7 per cent, respectively.

Weanling pigs of Poland China x Landrace x Duroc breeding were used. To determine the effect of the experimental treatments at different ages pigs were chosen by pre-experimental randomized selection to be sacrificed for carcass studies at 100, 150, and 200 pounds of body weight. Evaluating criteria were rate of gain, feed efficiency, weight, breaking strength and ash content of femurs, as well as phosphorus, calcium, magnesium, potassium, and sodium content of the femur ash. The effect of season upon the response of the experimental animals was studied by conducting two of the experiments outside during the summer and two inside during the winter.

A significant difference in average daily gain attributable to season occurred only from weaning to 100 pounds of body weight. However, significant differences attributable to season were more constant for breaking strength and ash content of femur, possibly indicating that sunlight furnished a factor(s) which enhanced calcium and phosphorus utilization other than irradiation of provitamin D in the animal's skin.

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<sup>1</sup>Doctoral thesis number 1685, submitted June 20, 1955.

Chairman of Committee, Damon Catron, Department of Animal Husbandry.

<sup>2</sup>B.S.A., University of Florida, Gainesville, M.S.A., *ibid*.

Graduate Assistant, Agricultural Experiment Station.

Flame spectrophotometric analysis revealed no significant difference in the calcium, potassium, magnesium, or sodium content of the femur ash. There was also no significant change in the phosphorus content of the femur ash attributable to season, replication, or treatment effect.

A multiple regression analysis indicated that 66.9-75.9, 75.9-92.7 and 75.0-88.5 per cent of the variability in average daily gain, breaking strength of femurs, and femur ash content, respectively, was attributable to variations in the dietary level of calcium and phosphorus. The values of *t* for test of significance for the standard partial regression coefficients indicated phosphorus to be much the more influential of the two elements regarding the response of the pigs to variations in the level of these elements in the experimental rations.

The dietary level of calcium and phosphorus needed to insure optimum rate of gain and skeletal response for swine fed antibiotic-supplemented rations appeared to be 0.8 and 0.6 per cent, respectively, for the 100 pound pig. The levels apparently may be reduced to 0.7 and 0.5 per cent for the 200 pound growing-finishing pig.

In order to further clarify the ramifications of the phosphorus requirements of growing swine, a study was conducted to determine if the source of dietary phosphorus influenced the response of growing-finishing pigs.

Two replicates of 18 pens of 4 pigs each (total 144 pigs) were fed in concrete dry lot to determine (1) the relative value of colloidal clay with soft phosphate, dicalcium phosphate and steamed bonemeal as phosphorus supplements for growing-finishing swine; (2) the effect of including these three supplements at two different levels in the rations; (3) the ability of the pig to utilize phosphorus of plant origin (phytin phosphorus); and (4) to determine the comparative nutritional value of organic and inorganic phosphorus for the growing and finishing pig.

Evaluating criteria were rate of gain, feed efficiency, breaking strength, weight and ash content of bone, as well as phosphorus, calcium, fluorine, potassium, sodium, and magnesium content of the femur ash. The dietary level of calcium and phosphorus was maintained at 0.7 and 0.5 per cent, respectively.

A comparison of feeding colloidal clay with either steamed bonemeal or dicalcium phosphate resulted in a significant decrease in rate of gain, feed efficiency, and breaking strength of femurs, accompanied by a significant increase in femur ash content and an increase in fluorine content of the femur ash from the pigs receiving the colloidal clay. There was no significant difference in the phosphorus content of bone ash or blood serum attributable to the type of phosphorus supplement. It appeared that a potential fluorine toxicological hazard was in the realm of possibility when colloidal clay was used as the phosphate source for the pig.

Growing-finishing swine did not utilize plant phosphorus as efficiently as inorganic phosphorus, as evidenced by a significantly poorer feed efficiency when the phosphorus level from the three supplements was decreased from 0.30 to 0.18 per cent of the ration. There was also a significant linear increase in average daily gains and feed efficiency when phosphorus from plant sources decreased from 0.50 to 0.35 to 0.20 per cent of the total rations, with inorganic phosphorus added to maintain 0.5 per cent phosphorus in the ration.

The data indicated that at least thirty per cent of the dietary levels of phosphorus recommended earlier should be furnished by an inorganic source. The inorganic source of phosphorus should preferably possess no potential toxicological qualities.

STRUCTURE OF MOLYBDENUM FILMS  
DEPOSITED ON SINGLE CRYSTALS OF SILVER AND ROCKSALT<sup>1</sup>Morris M. Christensen<sup>2</sup>

Department of Electrical Engineering

The purpose of this study was to investigate the orientation of molybdenum crystals in a thin film that had been prepared by vacuum evaporation on the (100) face of silver and rocksalt. Special consideration was given to the orienting, cutting, and polishing of the silver crystal prior to evaporation of the molybdenum film.

The silver crystal was mounted on a modified goniometer and a series of back-reflection Laue photographs was taken to determine the orientation of the crystal. Angular relations among the various zone axes in the crystal were read from a Geringer chart. True interzonal angles were measured by plotting the above angular relations on a Wulff net. Miller indices could be assigned to each zone in the photograph by comparing the angles that were measured on the plot with published values. The principal planes were identified in a similar manner.

As a check on the identification of the principal reflections the crystal was reoriented so that the X-ray beam was normal to the (100), (110), and (111) faces. When the X-ray beam was thus parallel to an axis of symmetry of the crystal, the corresponding angles were read on the circles of the goniometer. These angles are referred to as Euler angles.

With the orientation of the crystal known relative to a fixed reference frame, the specimen could be mounted in the Index Center of a precision milling machine and cut along a known crystallographic plane. The intermediate step between orienting and cutting the single crystal required the development of a transformation matrix. This matrix related the angles on the circles of the Index Center with the known orientation angles observed on the circles of the X-ray goniometer. Back-reflection X-ray photographs that were taken after cutting and electrolytically polishing the crystal surfaces confirmed the validity of the method.

Having obtained a crystal face of known configuration, experiments were undertaken to study the structure of thin molybdenum films evaporated onto the known surface. Molybdenum was evaporated from a 0.005 inch filament in a kinetic vacuum system and then condensed from the gas phase. First, the freshly cleaved cube face of a natural sodium chloride crystal was used as base for the condensed metal. Later the metal was condensed on the heat-treated (100) face of the silver crystal. Metallic films, 150 and 500 Angstrom units in thickness, were prepared by this method. The thickness of the deposited film was determined with a multiple-beam interferometer. When examined by electron diffraction, it was found that the crystallites in the deposited layer had the structure of metallic molybdenum, and were oriented in a completely random manner. The reflection pattern of the molybdenum film, 150 Angstrom units in thickness, showed several spots due to the silver crystal substrate.

<sup>1</sup>Doctoral thesis number 1728, submitted November 8, 1955. Chairman of Committee, W. B. Boast, Department of Electrical Engineering.

<sup>2</sup>B.S., University of Utah, Salt Lake City. M.S., University of Pittsburgh, Pittsburgh, Pennsylvania.  
Graduate Assistant, Industrial Science Research Institute.

SOME SURFACE PROPERTIES OF SEMI-IDEAL BINARY LIQUID MIXTURES<sup>1</sup>Sherril D. Christian<sup>2</sup>

Department of Chemistry

The surface behavior and activities of components in the systems acetic acid-trifluoroacetic acid, propionic acid-pentafluoropropionic acid and n-butyric acid-heptofluoro-n-butyric acid were studied at 20°C.

The dependence of surface tension on concentration was established for each of the three systems over the entire concentration range and represented by empirical analytic functions. An improved Wilhelmy-type film balance was designed for measuring surface tension of volatile liquids.

Vapor phase dimerization constants and heats of dimerization were determined for trifluoroacetic acid, pentafluoropropionic acid and heptofluoro-n-butyric acid in the vicinity of room temperature. The mixed dimerization constants for the dimer between trifluoroacetic acid and acetic acid and between pentafluoropropionic acid and propionic acid were determined at 25°C.

Activities of both components in the three systems were determined at 20°C using the method of Hansen and Miller. Analytic activity coefficient functions self-consistent according to the Gibbs-Duhem equation were determined.

A statistical treatment of the activities of components in a binary liquid mixture in which only the species A, F, A<sub>2</sub>, F<sub>2</sub> and AF are assumed to be present has been developed and successfully applied to the three systems.

A model of the surface phase has been invented to correlate activity and surface tension data. The following conclusions have been reached as to the structure of the surface phase:

1. In each system, surface molecules in the pure component are oriented perpendicular to the surface with the COOH group submerged.

2. The hydrocarbon acid molecules in mixtures always orient perpendicular to the interface with the COOH group submerged, and these molecules serve as "yardsticks" determining the thickness,  $\tau$ , of the surface layer. In the pure hydrocarbon acid the cross-sectional area of a surface molecule should be about  $20 \text{ \AA}^2$ , and in each system the thickness of the surface phase is  $(v_A/20) \text{ \AA}$ , where  $v_A$  is the molecular volume of A.

3. In the acetic acid system, molecules of both components have constant cross-sectional areas equal to  $v_i/\tau$ .

4. In the propionic acid and butyric acid systems, the fluorocarbon acid molecules tend to "lie down" in the surface layer when they are present in small concentrations. As the concentration of the fluorocarbon acid is increased, they interfere with each other and are forced to orient perpendicular to the surface. The effective area of the hydrocarbon acid is decreased as the concentration of the fluorocarbon acid is increased because the fluorocarbon acid molecules "wrap around" the terminal methyl group, thus reducing the space it occupies in the interface. In the butyric acid system this effect is sufficient to reduce the effective area of the hydrocarbon acid molecule in solutions of nearly pure perfluorinated acid to  $12 \text{ \AA}^2$ , essentially the area of the methyl group.

<sup>1</sup>Doctoral thesis number 1785, submitted May 15, 1956.

Chairman of Committee, Robert S. Hansen, Department of Chemistry.

<sup>2</sup>B.S., Iowa State College, Ames.

Research Assistant, Institute for Atomic Research.



RELATIONSHIPS OF GROUP E STREPTOCOCCI  
TO SWINE THROAT ABSCESSSES<sup>1</sup>John Raymond Collier<sup>2</sup>

Department of Veterinary Hygiene

Swine throat abscesses are the cause of serious economic losses to swine growers and meat packers in the United States. Three reports published during the past 15 years mention the isolation of Lancefield's Group E streptococcus from the exudate of lesions of that kind.

A cultural survey of the exudates of 492 swine throat abscesses revealed the Group E streptococcus to be associated with 85.6 per cent of those specimens. The incidence of that organism from specimens obtained from Ohio, Illinois, and Minnesota was quite similar to that of specimens obtained in Iowa.

Other kinds of bacteria recovered from some specimens were believed to be secondary, because of

1. The low over-all incidence of each kind.
2. The high over-all incidence (67.3 per cent) of pure cultures of the Group E streptococcus.
3. The frequent occurrence of the other kinds of bacteria in mixtures with the latter organism.

Throat abscesses were regularly induced in young swine given Group E streptococcus culture in feed. Intranasal or intrapharyngeal inoculation of that organism produced identical results; however, inoculation by various other routes failed to induce throat abscesses.

Pyrexia, leucocytosis, anorexia, and depression were clinical findings associated with the early stages of the throat abscess disease. The lymph nodes of the cervical region were found to be the sites of abscess formation.

The feeding of *Corynebacterium pyogenes* or *Pasteurella multocida* culture to swine did not result in throat abscess formation.

On the basis of the findings summarized above, it was concluded that

1. Lancefield's Group E streptococcus is the principal etiologic agent of the throat abscess disease of swine, and
2. It is an organism of limited pathogenic ability with a marked predilection for the nasopharynx and cervical region lymph nodes of swine.

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<sup>1</sup>Doctoral thesis number 1751, submitted December 9, 1955. Chairman of Committee, R. A. Packer, Department of Veterinary Hygiene.

<sup>2</sup>D.V.M., Ohio State University, Columbus. M.S., Iowa State College, Ames. Assistant Professor.

EVALUATION OF A TEST BATTERY FOR THE PREDICTION OF  
TENDENCY TO GRADUATE AND TENDENCY TO SEEK  
COUNSELING SERVICES OF THE TESTING BUREAU<sup>1</sup>

Chester Charles Collins<sup>2</sup>

Department of Vocational Education

In addition to the battery of freshman tests that all entering students at Iowa State College are required to take, 296 of these entering freshmen in September of 1950 were also administered a battery of aptitude, interest, and personality tests. Analysis of the usefulness of these tests was made after the completion of five calendar years. The group of 296 was reduced to 270 when 26 were eliminated from this study who were still in school or had temporarily withdrawn.

By September, 1955, 162 subjects or 60 per cent were graduated from some curriculum at Iowa State College. During this same period, 109 subjects, or approximately 40 per cent, had used the counseling services of the Testing Bureau. These two classifications provided the two criteria by which the usefulness of the freshman tests were evaluated. The first criterion was graduation tendency. The second criterion was the tendency to seek counseling services. These criteria are reasonably independent as determined by chi-square.

The variables chosen for the 270 engineering freshmen were the following:

American Council on Education Psychological Examination, Linguistic  
American Council on Education Psychological Examination, Quantitative  
High School Grade Point Average  
Owens-Bennett Test of Mechanical Comprehension  
Guilford-Martin Temperament Inventory of Factors G A M I N  
Guilford Temperament Inventory of Factors S T D C R

The relationships to the 14 variables were found by quadratic and linear discrimination with each criterion.

Quadratic discrimination with respect to the tendency to graduate yielded significant relationships at the 1 per cent level with the ACE-L score, ACE-Q score, high school grade point, Owens-Bennett Test, and the Guilford R scale score. Significant at the 5 per cent level was the Guilford Scale T score, and the Guilford-Martin Scale I score. The advantage with the four aptitude variables of quadratic discrimination over linear discrimination could not be demonstrated by the usual tests of significance.

A multiple prediction battery of the four aptitude scores (ACE-L, ACE-Q, Owens-Bennett Test, and high school average) yielded a coefficient of multiple correlation of 0.42, which is significant at the 1 per cent level. Subsequent tests of significance revealed the ACE-L score and the Owens Bennett score could be eliminated from the equation without significant loss.

If linear relationship is assumed between the personality factors and graduation, none of the ten scales yielded a significant relationship. With quadratic relationship, however, the Guilford T and Guilford-Martin I scales show significant relationship at the 5 per cent level with the criterion of graduation. The Guilford R scale scores are significantly related to the criterion of graduation at the 1 per cent level when quadratic relationship is assumed.

For purposes of this study, it was assumed that significance at the 1 per

<sup>1</sup>Doctoral thesis number 1801, submitted June 1, 1956.

Chairman of Committee, James E. Wert, Department of Vocational Education.

<sup>2</sup>Ph. B., Northwestern University, Evanston, Illinois. M.A., University of Illinois, Urbana. Counselor, College Testing Bureau.

cent level would be required before any attempt was made to include one of the ten personality variables in a prediction battery. With this 1 per cent level postulated, only the Guilford R scores needed to be considered in a multiple discrimination. Before inclusion in a multiple equation, however, these R scale scores had to be rectified. When the rectified scores for the Guilford R scale were included in a battery with the ACE-Q scores and the high school grade point averages, the coefficient of multiple biserial correlation of 0.4372 was obtained as contrasted to a correlation of 0.4004 without the rectified scores included. Using the 1 per cent level as a standard, the R scale rectified scores can be dropped, leaving the ACE-Q and high school average as predictors.

The second criterion in this study was the tendency to seek the counseling services of the Testing Bureau. The relationship of this tendency to each of the 14 variables was determined by quadratic and linear discrimination for the 270 engineering freshmen.

Significant linear relationships were found between the tendency to seek counseling services and the ACE-L score, the Guilford Scale C score and the Guilford-Martin I and N scores. With none of the fourteen variables was there a significant advantage of quadratic discrimination over linear discrimination.

A multiple prediction battery of the four foregoing significant variables yielded a coefficient of multiple biserial correlation of 0.2820. No significant loss ensued when the Guilford C score or when the Guilford I score was eliminated from the battery for predicting the tendency to consult the counseling services of the Testing Bureau. The remaining two-variable discriminant equation, consisting of the ACE-L score and the Guilford-Martin N score, yielded a coefficient of multiple biserial correlation of 0.2760. Neither of these variables could be eliminated without significant loss. The magnitude of the relationship between these variables and the tendency to seek counseling services indicated clearly that the identification of additional characteristics of students needs to be expanded to include other measures than aptitude test scores and person-trait scores such as are available from the Guilford-Martin Inventory.

It was concluded that each of the two criteria could be forecast from aptitude and personality test scores more effectively than by assigning to each student the average probability suggested by the experience of the 1950 entering engineering freshmen. The need is apparent for future studies to discover additional student characteristics for identifying engineering freshmen who will later graduate and those who will utilize the counseling services provided by the Testing Bureau of Iowa State College.

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CORRELATION OF PHOSPHORUS AVAILABILITY WITH THE  
QUANTITY OF SERUM ALKALINE PHOSPHATASE,  
BONE ASH AND GROWTH OF THE BABY PIG<sup>1</sup>

George E. Combs, Jr.<sup>2</sup>

Department of Animal Husbandry

The purpose of this study was to investigate the feasibility of using the blood serum alkaline phosphatase, skeletal and tissue composition, and growth rate of baby pigs as response criteria for evaluating the biological availability of the phosphorus contained in various phosphate supplements.

The average initial age and weight of the experimental pigs used throughout the course of this study was 8.1 days and 6.2 pounds, respectively. The data collected on the various criteria of response were statistically analyzed by the procedures commonly employed in parallel line assays.

A semi-synthetic ration, containing 0.07 per cent phosphorus, in which the major portion of the protein was supplied by Drackett Assay Protein C-1, blood fibrin, and gelatin was found to be more palatable than other rations which contained one or more of these proteinacious ingredients. Preliminary studies with the various response criteria, conducted in conjunction with the testing of rations, indicated that phosphatase activity, skeletal composition, and growth rate, but not the ash or phosphorus content of soft tissues, warranted further investigation.

Although there was observed to be a decline in phosphatase activity with age, this decline was found to be interrupted and replaced by a marked increase in activity when the pigs were fed rations considered to be inadequate in phosphorus. The phosphatase activity of pigs fed graded levels of phosphorus was shown to permit the establishment of a response curve in which only the linear regression component was statistically significant. The slope of this response curve, as determined by periodic observations of phosphatase activity, indicated that an experimental period of 24 to 28 days was required to give optimum results with pigs weaned at an average age of 8.1 days.

The data collected on the bone composition of pigs fed graded levels of phosphorus indicated that the per cent of ash, but not the per cent of phosphorus in the ash of the bones studied, gave results similar to those obtained with phosphatase activity. In addition to phosphatase activity and per cent bone ash, a linear response was obtained with the growth of pigs fed graded levels of phosphorus.

The phosphorus in steamed bone meal, as measured by the above mentioned response criteria, was shown to be less available than phosphorus in monocalcium phosphate ( $\text{CaH}_2\text{PO}_4 \cdot \text{H}_2\text{O}$ ) which was used in all experiments as the reference phosphate. The estimate of availability was observed to vary with the different response criteria. In comparison to per cent bone ash and growth rate, phosphatase activity was observed to be the least precise of the response criteria and overestimated the availability of phosphorus in steamed bone meal.

In addition to the response criteria previously used in this study, bone opacity as measured by the amount of light which passed through X-ray reproductions of these bones was used to evaluate the availability of phosphorus in dicalcium phosphate and colloidal phosphate.

The estimates given by phosphatase activity, growth rate, and bone opacity for the availability of the phosphorus in colloidal phosphate indicated it to be

<sup>1</sup>Doctoral thesis number 1693, submitted July 8, 1955.

Chairman of Committee, Damon Catron, Department of Animal Husbandry.

<sup>2</sup>B.S.A., University of Florida, Gainesville. M.S.A., *ibid*.

Graduate Assistant, Agricultural Experiment Station.



highly unavailable to baby pigs. The precision with which these response criteria evaluated phosphorus availability was observed to be approximately the same for all criteria.

The availability of phosphorus in dicalcium phosphate was observed to be equal to that of the reference phosphate when phosphatase activity and per cent femur ash were used as the response criteria. When bone opacity was used as the response criterion, the availability of the phosphorus in this supplement was found to be less than that of the reference phosphate. The estimate of availability obtained when growth rate was considered indicated the phosphorus in dicalcium phosphate to be considerably less available than the reference phosphate. This comparatively low estimate may be accounted for by assuming that the unthrifty condition of pigs in one pen, because of their failure to eat readily when weaned, exerted more influence on growth rate than on bone ash or femur opacity.

Although data were obtained which indicated that all of the previously mentioned response criteria could be used satisfactorily in evaluating sources of phosphorus, the criterion of choice appears to be dependent upon the degree of precision desired and the funds and equipment available.

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## PILOT PLANT EXTRACTION OF HAFNIUM FROM ZIRCONIUM<sup>1</sup>

Robert Payne Cox<sup>2</sup>

Department of Chemical Engineering

Zirconium has been used as a structural material in nuclear reactors because of its corrosion resistance, high-temperature strength, and low neutron absorption. Before zirconium can be utilized, however, the hafnium invariably accompanying it must be removed, since hafnium has a prohibitively high neutron absorption cross-section.

A process was developed for the production of hafnium-free zirconium by extraction of a zirconium nitrate solution with tributyl phosphate solvent. The hafnium content was reduced from about 2.5 per cent to less than 100 ppm. Particular emphasis was placed upon the following portions of the process: a) selection of the most economical method of preparing zirconium nitrate feed, b) demonstration of the use of a production type extraction unit, c) removal of hafnium-free zirconium from the solvent and regeneration of the solvent, d) recovery of nitric acid leaving the extraction apparatus, and e) conversion of the solution of purified zirconium to compounds suitable for metal production.

The preparation of zirconium nitrate feed solution was important to the extraction separation. Zircon sand was reacted with molten caustic soda and washed with water to remove soluble silicates and excess caustic. The best method tested for conversion of the washed reaction product was dissolution in sulfuric acid, leaving a residue of unreacted sands and silica. The filtered zirconium sulfate solution was converted to zirconium nitrate by precipitation of zirconium hydroxide and dissolution of the dried and washed hydroxide in nitric acid.

Hafnium-free zirconium was produced from the zirconium nitrate solution by solvent extraction with tributyl phosphate diluted with 40 volume per cent

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<sup>1</sup>Doctoral thesis number 1575, submitted July 12, 1954.

Chairman of Committee, G. H. Beyer, Department of Chemical Engineering. B.S., Virginia Polytechnic Institute, Blacksburg. M.S., Iowa State College, Ames. Graduate Assistant, Institute for Atomic Research.

heptane. The tributyl phosphate preferentially extracted the zirconium, leaving the hafnium and a majority of the minor impurities in the aqueous phase. A 14-stage mixer-settler extractor produced a zirconium extract of less than 100 ppm of hafnium and a raffinate of about 65 per cent hafnium. Zirconium was stripped from the tributyl phosphate with a sulfuric acid solution in a second extractor. The solvent was recycled to the extraction unit with periodic regeneration to restore extraction and settling characteristics. The nitric acid used in the extraction was recovered by evaporation of the aqueous streams leaving the extraction and stripping units. Zirconium sulfate was the residue from the evaporation.

The zirconium sulfate was converted to compounds suitable for reduction to metal. Zirconium oxide was made by precipitation of hydroxide from the sulfate solution and ignition of the filtered hydroxide to the oxide. This zirconium oxide could be converted to the tetrachloride and reduced with magnesium by the Kroll process. Or, zirconium tetrafluoride could be produced by reaction of the solid sulfate with aqueous hydrofluoric acid, and then reduced to the metal with calcium.

Preliminary cost estimates were made for production of hafnium-free zirconium compounds from zircon sand. The basis chosen was a plant producing 300,000 pounds of zirconium per year. Estimated chemical and total operating costs for zirconium tetrafluoride were \$0.90 and \$2.02 per pound of zirconium. Chemical and total operating costs estimated for zirconium oxide were \$0.64 and \$1.81 per pound of zirconium. In comparison, the estimates of chemical and total operating costs for zirconium oxide produced by the competing thiocyanate extraction process were \$1.34 and \$3.15 per pound of zirconium for a plant having one-half the annual capacity assumed in tributyl phosphate extraction.

Although the investigation was directed toward production of hafnium-free zirconium, much of the information obtained was applicable to manufacture of zirconium compounds without hafnium removal. Considerably wider use of zirconium would be possible should the cost of reduction to the metal be decreased.

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## HOW TENANT FARMERS IN THE SOUTH PLATTE VALLEY, COLORADO, ACCUMULATE CAPITAL AND OBTAIN FARMS<sup>1</sup>

John Calvin Crecink<sup>2</sup>

Department of Economics and Sociology

The basic purpose in this study was to examine two related problems: 1) Access to opportunities open to young men to begin farming as tenant operators; and 2) factors that influence the economic progress of tenants. The area selected for study was the South Platte Valley of Colorado. Farm tenancy has a long history in this area which has been relatively unaffected by governmental development programs. As such, the area appeared to provide an opportunity for study of the two problems under investigation. The sample of farms used in this study was drawn at random and data were obtained by interview of tenants who had operated as full tenants for at least one crop year before 1951.

<sup>1</sup>Doctoral thesis number 1796, submitted May 31, 1956. Chairman of Committee, John F. Timmons, Department of Economics and Sociology.

<sup>2</sup>B.S., Mississippi State College, Starkville. M.A., University of Virginia, Charlottesville.

The tenure trend in the area since 1940 has been characterized by increase in owner and part-owner operators and a decrease in tenants. The total number of farms has declined almost steadily since 1920, but the relative importance of the different tenure groups has shown a change in trend only since 1935.

During the early period of development of the South Platte Valley, the opportunity to enter farming was almost unlimited. Opportunities in recent times, however, have been much more restricted. Opportunities to enter farming currently range from entering as farm wage laborers to entering as owner-operators. Family assistance is becoming increasingly important in gaining access to the opportunity to begin as tenants. Even though the family does not own a farm upon which the beginning tenant can be located, parental assistance in the form of interceding with a neighboring landowner on the son's behalf, supplying machinery and equipment, arranging for credit, and supplying part of the management, is important in gaining access to farm operation. The opportunity to enter farming for the majority of the young men is as hired farm laborers. Family assistance also affects the relative bargaining positions of prospective tenants in obtaining farms. Since there is strong competition among prospective tenants for available rental farms in the area, young men without family assistance are at a disadvantage when bidding upon these rental farms.

Almost all tenants in this study expected to own farms eventually. The ownership of a farm was considered the principle means of achieving financial independence. However, most tenants could purchase an irrigated farm of only 40 acres in size providing not more than a 10 per cent down payment was required. Less than 10 per cent of the tenants could purchase an irrigated farm of 160 acres if a 50 per cent down payment was required.

Farmers, as do other businessmen, continually make decisions as to the use of their funds. Tenant operators with a given amount of funds available above consumption needs make decisions as to their use. The primary thesis presented in the study is that tenure progress is dependent to a large degree upon progress in capital accumulation--in other words, upon how these accumulated funds have been used.

The major quantitatively measurable factors affecting capital accumulation were put into a regression model. Size of the livestock enterprise, number of years experience as a tenant operator, size of farm, productivity of the farm, capital accumulation opportunity, age of operator, education of the operator, beginning capital and a measure of the leasing arrangement, explained 52.4 per cent of the variation in capital accumulation of tenant operators. Using only the first five of these factors, 51.2 per cent of the variation was explained. The chief factors in the regression analysis that affected capital accumulation in the order of their importance as determined by test of significance was the size of livestock enterprise, opportunity to accumulate capital, years of experience as a farm operator, productivity of the farm, and size of the farm.

Kind and type of lease, relationship to the landlord, and the occupational histories of the tenant operators were factors which affected capital accumulation of tenant operators but were not included in the regression analysis. These factors were examined through use of analysis of variance.

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SOME WAXY MUTATIONS IN MAIZE AND THEIR  
EFFECTS ON STARCH PROPERTIES<sup>1</sup>John H. Curme<sup>2</sup>

Department of Agronomy

A series of mutations at the waxy locus in maize was the subject of this study. The genetic mechanism inducing these mutations was the Activator-Dissociation system reported by McClintock. The mutations were identified by iodine titration of the endosperm starch. By this method good resolution was found between different samples analyzed.

A range of mutants was found from the normal waxy, containing no amylose in the endosperm starch, to the normal starchy composed of approximately 28 per cent amylose in the endosperm starch. Three intermediate classes of mutants were found whose starch was calculated to contain 20, 9, 3.42 per cent amylose, respectively. The frequency of these intermediate types was much higher than expected on the basis of their selection from the starchy and waxy phenotypes. The mutants isolated were grown and self-pollinated a second year to check their stability. The agreement of iodine titration values for the parent and progeny samples in the two years was found to be good.

A gene dosage study composed of all possible reciprocal crosses of the mutant types was undertaken in order to study the effects of the intermediate mutants on some physical properties of endosperm starch pastes and gels. The viscosity and gel strength measurements showed a partial dominance of the mutants conditioning higher amylose contents. The effects of the female parents in these crosses was greater than the effects of the male parents. Furthermore, a comparison was made between the gene dosage samples and mechanical mixtures of two starch sources, a starchy and a waxy type, blended to give comparable amylose percentages with those of the gene dosage samples. Viscosity and gel strength measurements of the starch pastes showed that even a small amount of amylose in the gene dosage samples had a large effect on the physical properties of starch pastes.

This was interpreted as a function of the structure and swelling of the individual starch granules. The amount of amylose and the length of amylose chains present is known to affect these properties of the granule. The starch granules of the gene dosage samples were homogeneous within each type while the granules of the mechanical mixtures were heterogeneous in type. It was concluded that the character of the granule types conditioned the differences in the gene dosage sample measurements. Furthermore, it was suggested that the different mutant types may effect specific properties of the endosperm starch pastes and gels.

<sup>1</sup>Doctoral thesis number 1714, submitted August 17, 1955. Chairmen of Committee, G. F. Sprague and I. J. Johnson, Department of Agronomy.

<sup>2</sup>A.B., Harvard College, Cambridge, Massachusetts. M.S., Kansas State College, Manhattan. Graduate Assistant, Agricultural Experiment Station.



IONIZATION DEFECT FOR ALPHA PARTICLES IN VARIOUS GASES<sup>1</sup>David W. Curtis<sup>2</sup>

Department of Physics

The ionization produced by the  $\text{Li}^{7*}$  and alpha particles from the reaction  $\text{B}^{10}(\text{n}, \alpha)\text{Li}^{7*}$  as they were stopped in argon, argon-nitrogen, and argon-carbon dioxide gas mixtures was measured. A gridded parallel-plate ionization chamber employing electron collection was used. Plutonium alpha particles were used for calibration and the ionization electron pulses were amplified and sorted with an electronic pulse height analyzer. The neutron source was a 300 kev linear positive ion accelerator utilizing the D-D reaction. The neutrons were thermalized by blocks of paraffin stacked around the chamber. The thin boron film was made by evaporating boron enriched to 95 per cent with  $\text{B}^{10}$  onto an aluminum backing. The gas mixtures were purified by continuous circulation over hot calcium-magnesium alloy.

The energies for the alpha particles and lithium recoils as calculated from the measured ionization yields were  $1.468 \pm 0.002$  and  $0.782 \pm 0.004$  Mev in argon,  $1.460 \pm 0.002$  and  $0.784 \pm 0.002$  Mev in argon plus 2 per cent nitrogen, and  $1.444 \pm 0.002$  and  $0.774 \pm 0.002$  Mev in argon plus 5 per cent carbon dioxide. The uncertainties quoted are the standard deviations for the series of measurements. These results should be compared to the energies  $1.473 \pm 0.002$  Mev for the alpha particles and  $0.841 \pm 0.002$  Mev for the lithium recoils determined from conservation of momentum. The 5 kev ionization defect measured for the alpha particles in argon was assumed to be due to source thickness. This leads to a 6 kev correction to be applied to all values obtained for the lithium recoils.

The results of this experiment along with those of other investigators demonstrate the constancy of the average energy required to produce an ion pair,  $W$ , for alpha particles in argon above an energy of 1.4 Mev. Further, ionization defects of  $8 \pm 3$  and  $24 \pm 3$  kev were obtained for the alpha particles from the reaction in argon plus nitrogen and in argon plus carbon dioxide, respectively. These results show the existence of a molecular defect for low energy alpha particles in the presence of polyatomic gases as suggested by the measurements of Herwig and Miller on fission fragments.

The ionization defect of about 50 kev obtained for the lithium recoils in argon gas is subject to considerable uncertainty due to conflicting evidence on the existence of ion recombination. This evidence would seem to indicate that there may be a fundamental difference between electron collection and total ion collection not as yet understood. Ionization defects of  $51 \pm 3$  and  $61 \pm 3$  kev were obtained for the lithium recoils in argon plus nitrogen and in argon plus carbon dioxide, respectively. The portion of each defect which may be attributed to the presence of a polyatomic gas can not be obtained from this experiment.

<sup>1</sup>Doctoral thesis number 1683, submitted June 14, 1955.

Chairman of Committee, Julian K. Knipp, Department of Physics.

<sup>2</sup>B.S., Western Michigan College, Kalamazoo.

Technical Assistant, Institute for Atomic Research.

THE NUCLEAR CHEMISTRY OF ANTIMONY AND TELLURIUM<sup>1</sup>Marion Clyde Day, Jr.<sup>2</sup>

Department of Chemistry

The techniques of scintillation spectrometry have been applied to the study of the radiations of two antimony and two tellurium isotopes. The Iowa State College 70 Mev synchrotron was used as an X-ray source to produce antimony 127 and antimony 129 by means of a ( $\gamma, p$ ) reaction on natural tellurium, and the ground state activities of tellurium 127 and tellurium 129 by means of a ( $\gamma, n$ ) reaction on natural tellurium. The energies of both the beta-rays and the gamma-rays have been measured, and where possible, coincidence studies have been made to determine the decay schemes of the isotopes. For the completed decay schemes, spin and parity assignments have been made, and these have been compared with the predictions of the shell model of the nucleus.

A method of isotopic enrichment was developed for the preparation of the tellurium beta-ray sources. This is based upon a change in chemical valence as the result of the recoil of a ( $\gamma, n$ ) reaction on the tellurium nucleus. For the preparation of both the tellurium sources and the antimony sources, the activities under study were purified by a second precipitation with hold-back carriers to prevent any serious contamination by other activities that might be present. In all cases the half life was followed as a check of the isotopic purity.

The 9.3 hour isomer of tellurium 127 was found to decay by a simple beta-ray with an end-point energy of  $0.683 \pm 0.010$  Mev. The log ft value was calculated to be 5.6. This indicates that the transition is of the allowed type and a spin change of  $\Delta I = 0$  or  $\pm 1$  and no change in parity would be expected. This is consistent with the proposed level assignments of  $d_{3/2}$  for the tellurium 127 and  $d_{5/2}$  for the iodine 127 ground states. The 72 minute isomer of tellurium 129 was found to decay by means of two beta-rays of  $1.46 \pm 0.01$  and  $1.01 \pm 0.02$  Mev and two gamma-rays of  $0.450 \pm 0.005$  and  $0.035$  Mev. Coincidence studies showed that the two gamma-rays are in coincidence, the 1.46 Mev beta-ray is in coincidence with the 0.035 Mev gamma-ray, and the 1.01 Mev beta-ray is in coincidence with the 0.450 Mev gamma-ray. The log ft values were calculated to be 5.8 for both of the beta-ray transitions which indicates that both of the transitions are allowed. A disintegration scheme and level assignments were proposed in which approximately 80 per cent of the transitions from the initial  $d_{3/2}$  state occur through the 1.46 Mev beta-ray to a level of spin either  $3/2$  or  $5/2$ . The remaining 20 per cent go through the 1.1 Mev beta-ray to a level of spin  $1/2$  followed by the 0.450 Mev gamma-ray to the same  $3/2$  or  $5/2$  level. The 0.035 Mev transition occurs in both cases to the  $g_{7/2}$  ground state of iodine 129.

The decay of the antimony 127 was found to be very complex. Three beta-ray groups were determined with end-point energies of  $1.57 \pm 0.03$ ,  $1.11 \pm 0.03$ ,  $0.857 \pm 0.021$  Mev, and eight gamma-rays were observed with energies of  $0.058$ ,  $0.185$ ,  $0.240 \pm 0.003$ ,  $0.456 \pm 0.004$ ,  $0.417$ ,  $0.563 \pm 0.005$ ,  $0.674 \pm 0.005$ , and  $0.764$  Mev. By means of coincidence measurements, it was found that the 0.674 Mev gamma-ray is in coincidence with the 0.857 Mev beta-ray, and the 0.240 and the 0.456 Mev gamma-rays are in coincidence with the 1.11 Mev beta-ray. Four gamma-rays with energies of  $0.165 \pm 0.005$ ,  $0.308 \pm 0.004$ ,  $0.534 \pm 0.003$ , and  $0.788 \pm 0.005$  Mev were observed in the

<sup>1</sup>Doctoral thesis number 1718, submitted September 2, 1955.

Chairman of Committee, A. F. Voigt, Department of Chemistry.

<sup>2</sup>B.A., San Jose State College, San Jose, California.

Junior Chemist, Institute for Atomic Research.

decay of the 4.2 hour antimony 129 activity. The end-point energy of the highest energy beta-ray group was found to be  $1.87 \pm 0.05$  Mev. Coincidence studies indicated a beta-ray group of 1.21 Mev in coincidence with the 0.788 Mev gamma-ray and a beta-ray of 1.47 Mev in coincidence with the 0.534 Mev gamma-ray. However, the intensities of the antimony 129 activities were too low to give statistically significant data for satisfactory coincidence studies.

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#### DETERMINATION OF SOIL TEMPERATURES FROM METEOROLOGICAL DATA<sup>1</sup>

Wayne Leroy Decker<sup>2</sup>

Department of Agronomy

Soil temperatures have an important effect on agriculture. They exert a control on the rate of germination and growth, on the activity of the soil's microbiological population, and on the weathering processes of the soil. Since soil temperatures are difficult to measure, there is a deficiency of soil temperature records. This work was instigated to provide a method for estimating soil temperatures from meteorological and soil factors.

Soil temperature observations were taken at three, six, twelve, and twenty-four inches below the surface with thermocouples. The measurements consisted of two daily temperature observations which were taken at each depth in each of three fallow and three grass plots. The dependent variables for the prediction analysis were the averages of the six daily observations.

Two models were used to obtain regression equations for prediction of the three inch soil temperature. In the first model, the air temperatures used as predictors were the temperature of the invading air  $T_u$ , defined as the upstream air temperature, and the temperature of the air twenty-four hours previous to the soil temperature observation  $T_1$ . The second model utilized the temperature of the air at the time of the soil temperature observation. In both regression analyses the daily solar energy  $S$ , the average night cloudiness  $C$ , the average wind velocity  $W$ , and the average soil moisture resistance  $M_s$  were used. The latter measurements were obtained from Bouyoucos soil moisture blocks.

For deeper soil levels the antecedent air temperatures were used as predictors. These antecedent temperatures were: for the six inch depth,  $T_3$  the air temperature three hours earlier than the observation time; for the twelve inch depth,  $T_4$  the air temperature ten hours earlier; and for the twenty-four inch depth,  $T_5$  the air temperature thirty-two hours earlier. The observed soil temperature at the next shallower depth and the average soil moisture resistance were also used as independent variables.

The air temperatures expressed as  $T_u$ ,  $T_1$ , and  $T_2$  were positively correlated with the three inch soil temperatures. From the three inch soil temperature analysis, which employed  $T_u$  and  $T_1$  as predictors, it was noted that  $T_1$  exhibited a greater effect on the soil temperature than  $T_u$ . When other factors were held constant a change of  $1^\circ\text{F}$  in  $T_1$  changed the three inch soil temperature by  $0.3^\circ$  to  $0.7^\circ\text{F}$ , while a change of  $1^\circ\text{F}$  in  $T_u$  only yielded a  $0.1^\circ$  to  $0.2^\circ\text{F}$  soil temperature change. From the analysis based on the second model, which used  $T_u$  and  $T_1$  along with the other variables as predictors,

<sup>1</sup>Doctoral thesis number 1745, submitted December 7, 1955.

Chairman of Committee, Don Kirkham, Department of Agronomy.

<sup>2</sup>B.S., Central College, Fayette, Missouri, M.S., Iowa State College, Ames.

explained a larger per cent of variability than the second model; but the increase in precision was so small that it does not appear worthwhile to employ the two variable models.

The daily total of calories of solar energy received was found to be positively correlated with the three inch soil temperature. When S was combined with the other independent variables, its effect did not vary a great deal. Each 100 calorie change in the daily solar energy was associated with a  $1^{\circ}$  to  $2.5^{\circ}\text{F}$  change in the three inch soil temperature.

Clouds occurring at night reduced the amount of energy lost by nocturnal radiation and increased the observed soil temperature. This effect was most pronounced during the warmer part of the year. An overcast night sky increased the three inch soil temperature the following afternoon by  $2^{\circ}\text{F}$  over the temperature which would have followed a clear night.

The average wind speed was negatively correlated with the three inch soil temperature during the warm portion of the year. Wind provides a mechanism for the mixing of the lower atmosphere and for heat removal from the surface. Average wind velocities of ten miles per hour reduced the three inch temperature as much as  $4$  or  $5^{\circ}\text{F}$  over a near calm condition.

According to these results the three inch soil moisture was not correlated with the three inch soil temperature during the winter and spring seasons. The failure in obtaining a significant relationship was due to the small variation in soil moisture during the cool seasons of the year. In summer and fall, when the variability was greater, lower soil moisture values were associated with higher soil temperatures. This negative relationship was due to the decrease in specific heat as the soil became drier.

For deeper soil levels the temperature of the next shallower depth was employed as a variable. The three inch soil temperature was used to predict the six inch soil temperature, the six inch soil temperature was used to predict that at twelve inches, while the twelve inch temperature was used as a predictor for the twenty-four inch depth. The temperatures at these shallower depths provided the best predictors for the soil temperatures at levels below three inches.

The simple correlation coefficients between the antecedent air temperatures and soil temperatures for depths below three inches were positive; but when expressed in terms of the partial regression coefficients, these relationships became negative. These negative values seem to indicate that a decreasing air temperature is associated with an increasing soil temperature.

This paradox is the result of the closer relationship between antecedent air temperature and the soil temperature at the shallower depth than on the temperatures at the depth under investigation.

For the levels below the three inch depth, soil moisture exhibited an erratic effect. It was usually positively correlated with the soil temperature of the same depth, but sometimes the correlation was negative. No physical explanation for this variation was found.

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PRESETTLEMENT FOREST TYPES IN IOWA<sup>1</sup>William Alexander Dick-Peddie<sup>2</sup>

Department of Botany

It is estimated that the presettlement vegetation of Iowa was 85 per cent prairie and only 15 per cent forest. These figures have been used as the basis for considering prairie to be the climax vegetation of the state. There are various reasons, however, for believing that forest is the true climatic climax of the area. It would be of the greatest value in the solution of this and other problems if it were possible to construct a picture of the presettlement vegetation of Iowa. This we have attempted to do for portions of the state by reference to the notations made during the original land surveys.

Surveyors were instructed to mark all section and quarter-section corners with posts, cairns, or other suitable markers. In addition they were required, whenever possible, to record the bearings and distances of two suitable trees, which were marked as witness trees to aid in relocating the corners. The species, by common names, size, and distance of these trees from the corners are recorded in the original surveyors' notes, filed in the Office of the Secretary of State in Des Moines, Iowa. Notes on trees falling in the surveyed line and on the general vegetation are included in these.

All witness and on-line trees recorded by the surveyors in three eastern Iowa counties, three township-wide belts east and west across southern, central, and northern Iowa, and 14 townships on the Des Moines and Missouri Rivers were tabulated. From these we attempted to form pictures of the species, average size, and density of forests in these areas.

A total of 15,291 trees was recorded in the areas studied. Thirty-six genera and species were recorded, with the smallest number in the northern county and transect, and the largest number in the southern. *Quercus* spp. made up about 67 per cent of all trees recorded. The average diameters of the trees in the counties comprising at least 2 per cent of the total, with the exception of *Ulmus* spp., were found to increase from north to south. *Quercus macrocarpa* was found to be the dominant species near the prairie-forest ecotone. It was also found to have a smaller average diameter and a larger average distance away from the corner than *Quercus alba* and *Q. velutina*, indicating oak-barrens vegetation and recent or current invasion.

The primeval forest cover in the areas studied appeared to be scattered, except for the oak-maple-linden communities, and to be evenly divided by rivers and streams. This uniform distribution suggests little effect of wind-sorted outwash or fire on forest distribution in these areas.

The mean diameters of the witness trees recorded in the township-wide transects showed a decrease to the north, and the percentage of trees falling on line decreased sharply in the same direction. There was found to be a definite decrease in a westerly direction of both mean diameters of the trees and percentage of trees falling on line.

The number of species recorded by the surveyors was less than the number now present. New species may have invaded the area in significant numbers in the 100 odd years since the surveys were made. Some of these could have been present in such small numbers, however, as to have been missed in the limiting sampling involved.

The data indicate: 1) that the forests of southeast Iowa were considerably older than those of the northeast corner of the state or of the western portions. Invasion appears to have been proceeding rapidly in the northeast and parts

<sup>1</sup>Doctoral thesis number 1687, submitted June 22, 1955.

Chairman of Committee, W. E. Loomis, Department of Botany.

<sup>2</sup>B.S., Drake University, Des Moines, Iowa.

of the west, as shown by oak-savannahs, whereas the forest-prairie ecotone was stabilized in the southeast. 2) Bur Oak (*Quercus macrocarpa*) and elm (*Ulmus americana*) appeared to be invaders of prairie areas. 3) On the basis of the climax concept of Weaver and Clements, the writer feels that the State of Iowa has an oak-hickory climax vegetation, with prairie being subclimax and oak-maple-linden post-climax.

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### INFLUENCE OF VARIOUS FACTORS ON THE PROTEIN REQUIREMENTS OF THE CHICK<sup>1</sup>

Gerald Alton Donovan<sup>2</sup>

Department of Poultry Husbandry

The protein requirements of the chick for maximum growth and feed efficiency and factors influencing these requirements have been studied. As an integral part of this evaluation, amino acid availability in certain proteins and the influence of the dietary protein level on liver fat content were also studied.

The chick's protein requirement on a semi-purified, glucose-soy protein diet was found to be approximately 25 to 26 per cent during the first 20 days after hatching. During the next ten-day period the protein requirement was shown to be approximately 22 per cent.

The type of carbohydrate in the diet appears to influence the chick's protein requirement during its first ten days of life. When starch was used as the carbohydrate during this period the chick's protein requirement for maximum growth was approximately 22 per cent. Substituting a monosaccharide, glucose, for the starch raised the requirements to about 26 per cent. By the time the chick was 21 to 30 days of age the influence of carbohydrate source on the protein requirement had disappeared.

The chick's protein requirement for maximum growth was about the same (26 per cent) during the 11 to 20 day age period on a diet containing either 975 or 1055 kilocalories of productive energy per pound. On a diet containing 720 kilocalories per pound there appeared to be a slight increase in growth with increments in dietary protein levels from 14 to 30 per cent. Increasing the density of the diet and the length of the feeding day did not enable the chicks to increase their total feed consumption enough to meet their energy needs.

Methionine appears to be the only limiting amino acid in soy protein of the three amino acids tested (methionine, glycine, and tryptophan).

The essential amino acids, with the exception of tryptophan and glycine, in soy protein and in a casein-soy protein combination were tested for their relative utilization by the chick. The availability of these amino acids was based upon the ratio of the content of each amino acid in the diet to the content of each corresponding amino acid in the excreta. The amino acid contents were determined by microbiological analysis.

These amino acids differed in their availability within and between protein sources. Arginine appeared to be the most readily available and threonine the least available in both the soy protein and the casein-soy protein combination.

Free arginine, lysine, and methionine when added to a corn-meat scraps diet were more completely utilized by the chick than the corresponding

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<sup>1</sup>Doctoral thesis number 1688, submitted June 24, 1955. Chairmen of Committee, S. L. Balloun and R. E. Phillips, Department of Poultry Husbandry.

<sup>2</sup>B.A., University of Connecticut, Storrs. M.S., *ibid.* Graduate Assistant, Agricultural Experiment Station.

protein-bound amino acids. The addition of each of these three synthetic amino acids increased the chick's ability to utilize protein-bound amino acids.

The chick's liver fat content was not affected by the energy level of the diet, but increasing the dietary protein level from 14 to 30 per cent caused a decrease in liver fat.

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## PHYSICAL SYSTEMS WITH TIME VARYING PARAMETERS<sup>1</sup>

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Department of Electrical Engineering

The purpose of this study was to investigate the behavior of time varying systems, and to extend, if possible, some of the concepts and methods used in fixed system analysis to the time varying case. A linear time varying system has been defined as any system in which one or more of the parameters of the system vary independently according to some known function of time. Particular emphasis has been placed on the case where the system employs feedback, and where the variations of the parameters are periodic functions of time.

The concept of system function as used by earlier writers in this field has been employed as the basis for analysis, but the method of obtaining the system function is different and it is felt more suitable for a physical interpretation. The system function,  $H(s, t)$ , may be thought of in two ways; first as the Laplace transform of the impulsive response,  $W(t, \lambda)$ , with respect to the age variable,  $\lambda$ , and secondly to an input of the form  $e^{st}$  divided by that input. The second concept of the system function is a convenient one for the cases where systems are cascaded or where the systems involve feedback. In this study, an expression for  $H(s, t)$  as an integral was found from the system differential equation. This form is convenient for determining the over-all system function for cascaded systems from the constituent parts.

If the system function of a system is known, the output in the time domain for any arbitrary input may be found from an inversion integral or by reference to a table of Laplace transforms in the same manner as for fixed systems, so that the central problem in the analysis of time varying systems is the determination of the system function.

The inverse system function is a useful concept in the analysis of time varying systems and may be thought of as the input to the system necessary to cause an output  $e^{st}$  divided by that output. The inverse system function occurs particularly in the case of feedback systems, and like the system function may be found from the system differential equation as an integral.

The system function of a system consisting of several constituent systems and involving feedback may be found by operations involving the system functions and inverse system functions of the several constituent systems. The stability of such a system can be determined by observing the  $s$  plane behavior of the system function in a manner similar to that for fixed systems with one important difference in that the singularities of the system function may in general be functions of time, and hence may move about in the  $s$  plane.

For the case where the parameters of a time varying system vary periodically all having the same period, it has been found that the system function of

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<sup>1</sup>Doctoral thesis number 1748, submitted December 8, 1955. Chairman of Committee, George R. Town, Department of Electrical Engineering.

<sup>2</sup>B.S., State University of Iowa, Iowa City. Assistant Professor.

such a system is also periodic in time having the same period as the parameters of the system. It has been found also that the poles of such a system function occur in families having the same real part, but having imaginary parts which differ by integral multiples of the angular frequency of the system. The stability of such a system is determined from the location of the real parts of the poles of the system function. The real parts of the poles are the same as those of the characteristic exponents of the set of linearly independent solutions to the homogeneous system differential equation.

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## ORIENTATION IN NITRATION OF AROMATIC NITRILES<sup>1</sup>

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Department of Chemistry

The nitration of benzonitrile has been carried out in perchloric acid solutions with fuming nitric acid at temperatures of 25°, 35°, and 43°. The per cent m-nitrobenzonitrile and the ratio of o-nitrobenzonitrile to p-nitrobenzonitrile have been determined quantitatively by an infrared spectroscopic method.

The nitration product obtained under the various conditions was found to contain from 72 to 83 per cent m-nitrobenzonitrile. The low values were obtained from runs which were allowed longer reaction time and in which, therefore, some side reactions may have occurred. The temperature differences apparently had not effect on the per cent m-nitrobenzonitrile formed.

The ortho to para ratio observed was greater than two and the range was 3.3 to 3.7. No significant change in the ortho to para ratio due to change of reaction temperature was observed.

It is concluded that the nitrile group like the nitro and carboxyl groups is a meta-ortho directing group and that the ortho direction is due to the electronic influences rather than to steric influences of the latter two groups.

Attempts to determine the isomer ratio obtained in the nitration of 2,5-dichlorobenzonitrile failed because no effective nitration conditions in which hydrolysis of the nitrile group did not occur could be found. 2,5-Dichloro-4-nitrobenzonitrile and 2,5-dichloro-6-nitrobenzonitrile were prepared and their infrared spectra determined.

Attempts to determine the isomer ratio obtained by methods other than infrared spectroscopy led to a study of the hydrogenation of the nitrobenzonitriles. It was found that the catalytic hydrogenation in absolute ethanol at room temperature and atmospheric pressure of m-nitrobenzonitrile and p-nitrobenzonitrile gave the corresponding aminonitriles, but o-nitrobenzonitrile gave quantitative yields of o-aminobenzamide. A possible mechanism for this reaction has been given.

Although the formation of o-aminobenzamide was quantitative, several methods of determining it in the presence of the hydrogenation products of m- and p-nitrobenzonitrile failed. These failures were due to the relatively small quantity of o-aminobenzamide present in the mixture. Methods tried included an infrared spectroscopic method for o-aminobenzamide in chloroform solution, nonaqueous titration of the hydrogenation products as bases,

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<sup>1</sup>Doctoral thesis number 1690, submitted June 28, 1955.

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<sup>2</sup>B.A., Newcomb College, New Orleans, Louisiana. M.S., Tulane University, New Orleans, Louisiana. Graduate Assistant, Industrial Science Research Institute.



and the hydrolysis and determination of o-aminobenzamide as anthranilic acid by precipitation and titration of zinc anthranilate.

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EFFECTIVENESS OF USING BIOGRAPHICAL SKETCHES  
IN THE TEACHING OF HIGH SCHOOL CHEMISTRY<sup>1</sup>

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Department of Vocational Education

The purpose of this study was to reveal objective evidence regarding the effectiveness of using biographical sketches in the teaching of high school chemistry.

For purposes of this study, the control-group sample consisted of 50 high school senior boys and 30 high school girls, as did the experimental-group sample. The experimental group excelled the control group in mean IQ by the nonsignificant amount of 0.9 IQ points, whereas the experimental group was inferior to the control group in mean geometry mark by the nonsignificant amount of 0.5 grade points. Neither group was highly atypical when compared with Kuder norms of scientific interest or with national norms for IQ's of high school seniors.

All students in the control and experimental groups took chemistry at Ames High School, Ames, Iowa, in the same classroom and with the same teacher. During the experiment the time available for each chemistry unit was the same for each group. Teaching methods were the same with the exception that in the experimental group men and events in chemistry were emphasized by the presentation of biographical sketches and in the control group no such emphasis occurred.

Evaluated in this study were six objectives of the high school chemistry course as follows:

Fundamentals of high school chemistry	Scientific method
Men and events in chemistry	Scientific attitude
Science activities and ambitions	Scientific interest

For five of the six objectives, the exception being the objective of scientific interest, mean differences between the experimental and control groups were tested by the analysis of covariance technique. The IQ and geometry mark were control variables in the analysis of covariance tests of significance and stratification was on the basis of sex.

The criterion for the evaluation of achievement in fundamentals of chemistry was the total score on seven objective unit tests. If the IQ's and the geometry marks were controlled, the students with increased emphasis on biographical sketches exceeded students in the control group by three-fourths of a standard score unit. A student making normal progress without biographical sketches would shift from the 50th percentile rank to the 78th percentile rank with increased emphasis upon biographical sketches, as indicated by the sample of students here considered.

It was unexpected to find the magnitude of the effectiveness so great when evaluated in terms of achievement in the fundamentals of chemistry since the

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<sup>1</sup>Doctoral thesis number 1786, submitted May 18, 1956. Chairman of Committee, James E. Wert, Department of Vocational Education.

<sup>2</sup>B.A., Drake University, Des Moines, Iowa. M.S., *ibid*.

time spent with biographical sketches reduced the class time spent in other learning activities.<sup>6</sup> With regard to the foregoing objective, both boys and girls profit from the use of biographical sketches and they profit equally.

The criterion for the evaluation of achievement in men and events in chemistry was limited to the score on a 53-item, multiple-choice test designed for that purpose. If the control and experimental groups had identical mean IQ's and mean geometry marks, students with increased emphasis on biographical sketches, on an average, would have excelled students in the control group by 0.98 of a standard score. Thus, a student making normal progress who would be in the 50th percentile rank in the control group, would be in the 84th percentile rank in a group with increased emphasis upon biographical sketches.

It was not unexpected to find evidence in this study that the use of biographical sketches increases the achievement in men and events in chemistry since in the experimental group 14 per cent of the available class time was used for emphasis on such information. With regard to the foregoing objective, both boys and girls profit from the use of biographical sketches and girls profit more than boys.

The criterion for the evaluation of achievement in scientific method was limited to the score on a 23-item, multiple-choice test designed for that purpose. No significant t-values resulted from the analysis of covariance used to test the difference in the means of the control and experimental groups with regard to achievement in scientific method. The findings of this study did not tend to substantiate the point of view that emphasizing biographies increases knowledge of the scientific method.

The criterion for the evaluation of scientific attitude was limited to the score on a 31-item, multiple-choice test designed for that purpose. In this evaluation, the control group, without biographical sketches, excelled the experimental group by an amount which yielded a significant t-value, at the 5 per cent level of confidence, in the analysis of covariance. Although some chemistry teachers have maintained stressing biographical information increases achievement in scientific attitude there was insufficient evidence in the findings of this study to substantiate that point of view.

The criterion for the evaluation of scientific interest was the shift in scientific interest before and after chemistry instruction. The Kuder Preference Record, form CH, furnished the required information. The difference between a pre-test and a post-test automatically controls on individual differences among the students. A positive mean change-in-interest score, demanded by the null hypothesis, produced a t-value of 4.35, highly significant at the 1 per cent level. The inference that greater scientific interest results from high school chemistry instruction seems justified. Increased emphasis on biographical sketches was not demonstrated to produce greater scientific interest.

The criterion for the evaluation of achievement in science activities and ambitions was the total score on a questionnaire which consisted of 4 items with regard to 1) reading of science articles, 2) rating of high school chemistry, 3) college plans, 4) college major. Individual differences among the students in science activities and ambitions as here measured, and as tested for significance by the analysis of covariance, were not demonstrated to be a function of the emphasis on biographical sketches. As would be expected, boys are more interested than girls in science activities and ambitions as indicated by a t-value of 4.33, significant far beyond the 1 per cent level.

In searching for objective evidence regarding the effectiveness of using biographical sketches in the teaching of high school chemistry, it was demonstrated by this study that an increased emphasis upon biographical sketches results in an increase of 1) achievement in fundamentals of chemistry and 2) achievement in men and events in chemistry. It was not demonstrated in this study that an increased emphasis upon biographical sketches results in an increase in 1) achievement in scientific method, 2) scientific attitude, 3) scientific interest, and 3) science activities and ambitions.

Implications for the teaching of high school chemistry, resulting from the conclusions and discussion in the evaluation of the six objectives studied, include the desirability of emphasis upon biographical sketches in high school chemistry instruction.

## ORIENTATION REACTIONS OF PHENOXATHIIN AND ITS DERIVATIVES<sup>1</sup>

Scott H. Eidt<sup>2</sup>

Department of Chemistry

In the course of determining the positions in phenoxathiin (I) affected by common reagents it was necessary to identify substitution products and to synthesize some of these compounds by unambiguous methods. The technical complications resulting from the simultaneous formation of mono- and di-substitution products made difficult a rigid comparison of the relative directive influence of the oxygen and sulfur atoms.

After treatment of I with one equivalent of *n*-butyllithium (II), followed by carbonation, there were obtained pure 4-phenoxathiincarboxylic acid (1), m.p. 171-173°, and 1,6-phenoxathiindicarboxylic acid, m.p. ca. 350° (decomp.), in yields of 36.9 per cent and 1.4 per cent, respectively. When two equivalents of II were employed there resulted 1,6- and 4,6-phenoxathiindicarboxylic acid, m.p. 266-267°, in yields of 8.9 per cent and 34.7 per cent, respectively. The dimethyl esters of the 1,6- and 4,6-diacids melted at 150.5-151.5° and 82.5-83°, respectively. The structures of the 1,6- and 4,6-diacids were proved when the acids were desulfurized by Raney nickel to yield 2,3'- and 2,2'-dicarboxydiphenyl ether, respectively.

Only monometalation was reported when I-10-dioxide was treated with 1.5 equivalents of II at 0° (2). Upon repetition of the experiment, there were obtained, subsequent to carbonation, 1-phenoxathiincarboxylic acid 10-dioxide, m.p. 230-232°, and 1,9-phenoxathiindicarboxylic acid 10-dioxide, m.p. 350-352° (decomp.), in yields of 14.9 per cent and 48.1 per cent, respectively. The dimethyl and diethyl esters of the 1,9-diacid melted at 170-171° and 143-143.5°, respectively. Desulfurization of the 1,9-diacid by Raney nickel to 3,3'-dicarboxydiphenyl ether proved that I-10-dioxide was dimetalated in the 1,9-positions.

Cleavage, reduction and metalation occurred when I-10-oxide was allowed to react with II. The extent of each reaction depended upon several variables. After carbonation of a low temperature reaction mixture there were obtained I, *n*-butyl mercaptan, diphenyl ether, 2-carboxydiphenyl ether, 2,2'-dicarboxydiphenyl ether and 1-phenoxathiincarboxylic acid. The last product was the only one reported when the experiment was carried out at a higher temperature (2). In order to test a proposed mechanism for the metalation reaction, I-10-oxide was treated with a mixture of 2-lithio- and 2,2'-dilithio-diphenyl ether and the reaction mixture was carbonated. The isolation of a small amount of 1-phenoxathiincarboxylic acid 10-oxide gave support to the postulated mechanism.

2-Aminophenoxathiin-10-dioxide, m.p. 169-176°, 175-176°, was prepared from 2-nitrophenoxathiin-10-dioxide by a published procedure (3). The amine

<sup>1</sup>Doctoral thesis number 1752, submitted December 9, 1955.

Chairman of Committee, Henry Gilman, Department of Chemistry.

<sup>2</sup>B.S., Southern Methodist University, Dallas Texas.

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was converted to 2-chloro-, 2-bromo-, m.p. 177-178°, and 2-iodiphenoxathiin-10-dioxide, m.p. 171-172°. Iodination of I-10-dioxide also yielded the last compound.

I-10-dioxide, 2-chloro- and 2-bromophenoxathiin-10-dioxide were reduced by lithium aluminum hydride to I, 2-chloro- and 2-bromophenoxathiin, respectively. The last compound was also prepared from 2-aminophenoxathiin. The melting point of 2-bromophenoxathiin was ca. 30° higher than that reported (4).

Attempts to prepare 2-bromophenoxathiin by a published bromination procedure (4) were unsuccessful. Chlorination of I by sulfuryl chloride yielded 3-chlorophenoxathiin, m.p. ca. 80°, and a   , -dichlorophenoxathiin, m.p. 168-169°. It was proved that both chlorination of I and the reaction of 3-chlorodiphenyl ether, sulfur and aluminum chloride (5) produced 3-chlorophenoxathiin.

I-10-oxide was prepared in yields of 93 per cent and 95 per cent by oxidation of I in glacial acetic acid with dilute nitric acid. Also prepared by this oxidation procedure was 4-phenoxathiincarboxylic acid 10-oxide, m.p. 171-173°.

The following compounds were prepared by oxidation with 30 per cent hydrogen peroxide: 1-phenoxathiincarboxylic acid 10-oxide, m.p. 262° (decomp.), 1,6-phenoxathiindicarboxylic acid 10-dioxide, m.p. 351-353° (decomp.), 4,6-phenoxathiindicarboxylic acid 10-dioxide, m.p. 329-331° (decomp.), 2-bromophenoxathiin-10-dioxide and 4-bromophenoxathiin-10-dioxide, m.p. 157.5-158°.

The hypochlorite oxidation of 2,8-diacetylphenoxathiin yielded 2,8-phenoxathiindicarboxylic acid 10-dioxide, m.p. 392-394° (decomp.). The results were in contrast to those of the workers (4) who reported the preparation of 2-phenoxathiincarboxylic acid from 2-acetylphenoxathiin by this method.

A carbon-sulfur bond in I was cleaved by lithium in refluxing ether. Hydrolysis of the cleavage product yielded 2-thiodiphenyl ether, m.p. 67-68°, an authentic specimen of which was prepared from sulfur and 2-lithiodiphenyl ether. The thiol was oxidized to bis-(2-phenoxyphenyl) disulfide, m.p. 75-76°, and was converted to 2-phenoxyphenylmercaptoacetic acid, m.p. 126.5-127°, by reaction with chloroacetic acid. Carbonation of the product of lithium cleavage of I yielded 2-carboxy-2'-thioldiphenyl ether, m.p. 142-143°, and its disulfide, m.p. 235-235.5°.

The results indicate that competition between the directive influences of the ether and thioether linkages may prevent substitution exclusively in one position.

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COMPARISON OF PHENANTHRIDINE WITH  
OTHER AZA-AROMATIC HETEROCYCLES<sup>1</sup>John Joseph Eisch<sup>2</sup>

Department of Chemistry

Contrasted with other aza-aromatic heterocycles such as pyridine and quinoline, the fundamental chemistry of the phenanthridine system has been largely neglected. This nitrogen isoster of phenanthrene recently has attained physiological significance due to the trypanocidal and bacteriostatic properties of certain derivatives. Moreover, recent theoretical predictions of the orientation and reactivity of aza-aromatic substitution processes necessitate experimental data to test the validity of the viewpoint. Consequently, the present study was undertaken to elucidate the chemistry of phenanthridine and certain of its derivatives. In conjunction with this, a comparison of the known chemistry of aza-aromatic heterocycles was carried out in order to evaluate the relative ease of reaction, probable reaction mechanism, and agreement of experimental findings with theoretical predictions for these systems.

A rationalization of the chemical behavior of these aza-aromatic systems was developed in terms of modern views of molecular structure and chemical reactivity. The following general conclusions can be drawn. First, the overall reactivity of aza-aromatic heterocycles toward electrophilic and nucleophilic attack increases in the order: pyridine < quinoline  $\approx$  isoquinoline < acridine  $\approx$  phenanthridine. Second, the site of nucleophilic substitution will be the carbon atom of lowest charge density ( $C_6$  in phenanthridine), and electrophilic reagents will tend to attack positions of high charge density. Third, where there are several positions of high charge density such as  $C_2$ ,  $C_4$ ,  $C_8$ , and  $C_{10}$  in phenanthridine, the site of electrophilic substitution may be determined by the polarizability of the site and the localization energy of that position. Fourth, experimental factors such as the specific nature of the reagent, solvent, acidity, catalyst, and temperature can exert a profound influence on the rate and course of substitution. Fifth, as one passes through the series from pyridine to phenanthridine, not only do alpha-substituted derivatives become more reactive, but the keto tautomer of alpha hydroxy derivatives becomes more stable than the hydroxyl form, and the dihydro derivatives become more resistant to oxidation.

Experimentally, the chemistry of phenanthridine, phenanthridone, and certain of their derivatives was studied in order to enable a direct comparison with other aza-aromatic heterocycles. Thus, the behavior of phenanthridine toward certain electrophilic and nucleophilic reagents was considered and the following observations made.

First, the azomethine linkage has a high order of reactivity toward organometallic reagents: 1) *n*-butyllithium gave a 90 per cent yield of 6-*n*-butylphenanthridine (b.p.  $177^\circ/3.4$  mm); 2) *n*-propylmagnesium bromide afforded 84 per cent of 6-*n*-propylphenanthridine (b.p.  $163^\circ/1.9$  mm); 3) *o*-tolyllithium yielded 74 per cent of 6-*o*-tolyl-5,6-dihydrophenanthridine (m.p.  $140.5^\circ$ ) which was dehydrogenated to the 6-*o*-tolyl derivative (picrate, m.p.  $167.5^\circ$ ); 4) benzylmagnesium chloride gave 6-benzyl-5,6-dihydrophenanthridine (m.p.  $127^\circ$ ) oxidizable to 6-benzoylphenanthridine (m.p.  $152^\circ$ ). 6-*n*-Propylphenanthridine (picrate, m.p.  $196^\circ$ ) and 6-*n*-butylphenanthridine (picrate, m.p.  $195.5^\circ$ ) were synthesized unambiguously from 2-butyrambinobiphenyl (m.p.  $86^\circ$ ) and 2-valeraminobiphenyl (m.p.  $73^\circ$ ), respectively, by cyclization with phosphorus oxychloride.

<sup>1</sup>Doctoral thesis number 1771, submitted March 9, 1956.

Chairman of Committee, Henry Gilman, Department of Chemistry.

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Second, other anionic reagents such as cyanide and hydroxyl ions also attacked phenanthridine with facility. Treatment of phenanthridine methiodide with potassium cyanide and subsequent oxidation of the product with iodine provided 6-cyanophenanthridine methiodide (m.p. 163°) in 90 per cent yield. Likewise, heating phenanthridine with fused potassium hydroxide converted it to phenanthridone in 67 per cent yield.

Third, the system was brominated and sulfonated rather readily. The use of N-bromosuccinimide or other reagents gave a moderate yield of 2-bromophenanthridine (m.p. 162°), picrate (m.p. 251°). This compound was converted to the 2-cyano derivative (m.p. 216°). On the other hand, fuming sulfuric acid at 90° gave a high yield of two or more sulfonic acids. The less soluble acid was shown to be a monohydrate and may be the 4-isomer.

The dichromate oxidation of 6-methylphenanthridines to phenanthridones yielded interesting by-products. The yellow solid (m.p. 301°) from 2-bromo-6-methylphenanthridine seems to be di-(2-bromo-6-phenanthridyl) glyoxal. Other alkyl derivatives gave ketones in addition to phenanthridone: 6-*n*-butylphenanthridine led to 6-butyrylphenanthridine (m.p. 108°), 2,4-dinitrophenylhydrazine (m.p. 158.5°), picrate (m.p. 198°); and 6-*n*-propylphenanthridine yielded 6-propionylphenanthridine (m.p. 73°), 2,4-dinitrophenylhydrazine (m.p. 225.5°), picrate (m.p. 195.5°).

The substitutional chemistry of phenanthridone was studied in an analogous fashion. This cyclic amide was readily halogenated to yield the 2-bromo- (m.p. 328.5°), 2-chloro- (m.p. 327°) and 2-iodophenanthridone (m.p. 323.5°). That phenanthridone gives 4-nitrophenanthridone (m.p. 263°) as the minor product of nitration was verified by spectral studies and synthesis. Attempted acetylation and mercuriation were unsuccessful, but the system could be sulfonated quantitatively to give phenanthridone-2-sulfonic acid (toluidine salt, m.p. 283°). The prolonged action of *n*-butyllithium on phenanthridone gave 6-*n*-butylphenanthridine (as picrate, m.p. 195.5°).

In addition, the following phenanthridone derivatives were prepared: 2-acetamino- (m.p. 358°); 2-acetamino-*x*-bromo- (m.p. 286°); 2-acetamino-*x*-nitro- (m.p. 353.5°); 2-chloro-5-methyl- (m.p. 192°); 5-methyl-2-nitro- (m.p. 249°); 2-bromo-4-nitro- (m.p. 284°); 2-chloro-4-nitro- (m.p. 280°); and the 2-carboxylic acid (m.p. 361°).

A comparative study was made of the reactivity of certain aza-aromatic heterocycles and anils toward allylmagnesium bromide. The results are given in Table 1.

Table 1. Reaction of allylmagnesium bromide with compounds containing the azomethine linkage

Reactant	Product	Yield %	B.p.	(M.p.)
Pyridine	4-Allyl-	9	186-188°	(730 mm)
Phenanthridine	6-Allyl-5,6-dihydro-	78	174-177°	(3.6 mm)
Benzalaniline	$\alpha$ -Allylbenzylaniline	80	146-148°	(2.9 mm)
Acridine	9-Allyl-9,10-dihydro-	81	---	(115-116°)
Quinoxaline	2,3-Diallyl-1,2,3,4-tetrahydro-	86	142-143°	(1.8 mm)
Benzophenone anil	$\alpha$ -Allylbenzhydryl-aniline	95	---	(78.5-80°)

In all cases 1,2 addition to the azomethine linkage occurred, except for pyridine and acridine where 1,4 addition took place. The proof of structure of 4-allylpyridine (picrate, m.p. 167.5°) was accomplished by catalytic hydrogenation to 4-*n*-propylpyridine (picrate, m.p. 128°) and comparison with an authentic sample of the latter. Moreover, 2-allylpyridine (b.p. 63°/12 mm) (picrate, m.p. 118.5°) was unambiguously synthesized and shown to differ from the above product. That 1,2 addition occurred with benzophenone anil was demonstrated by reducing  $\alpha$ -allylbenzhydrylaniline to  $\alpha$ -*n*-propylbenzhydrylaniline (m.p. 85°) and synthesizing the latter compound unequivocally from butyrophenone anil (b.p. 182°/13 mm) and phenyllithium.

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ANALYSIS OF FACTORS AFFECTING PRODUCTION AND WHISTLING  
BEHAVIOR OF THE EASTERN BOB-WHITE, *COLINUS V. VIRGINIANUS* L.,  
IN DECATUR COUNTY, IOWA<sup>1</sup>

James Bruce Elder<sup>2</sup>

Department of Zoology and Entomology

An investigation was made of Eastern Bob-white, *Colinus v. virginianus* L., nesting and production in 1954 and 1955, and of changes in cover and land-use patterns from 1941 to 1950 on the 7713-acre Decatur County Quail Research Area in south-central Iowa in an attempt to determine the cause, or causes, of depressed populations (relative to 1935-1944) since 1941. Concurrent studies of bob-white whistling behavior were made to determine the daily and seasonal whistling patterns of male bob-whites in relation to changes in weather, nesting phenology, and individual behavior.

Nesting and brood data were gathered by intensively searching for nests and broods on a representative 400-acre portion of the Decatur Area and by follow-up of observations of farmers on the Decatur Area. Fifteen nests were examined in 1954 and two in 1955. Three 1954 nests were located in herbaceous native pasture, four in brush pasture, four in roadside ditches, two in fallow sites, one in a field edge, and one on the edges of a drainage ditch. Nine nests contained eggs ranging from one to twenty-four per nest. Seven complete clutches ranged from nine to nineteen eggs, averaging 14.3, standard deviation  $\pm 3.5$ . Three successful nests hatched sixteen of seventeen eggs, nine of ten, and eight of thirteen, respectively. Causes of nest failure were desertion (seven nests), predation (three nests), mowing of hayfields and roadsides (two nests). One 1955 nest was located in brush pasture and hatched ten of twelve eggs. The other was located in brome-alfalfa hay and contained fifteen hatched eggs when found.

Data were obtained for twenty-one broods in 1954 and fourteen broods in 1955. Thirteen 1954 broods averaged 10.6, standard deviation  $\pm 3.1$ . Four 1955 broods contained nine, thirteen, fifteen, and fifteen birds, respectively.

The fall bob-white potentials of 119 north Decatur Area forties were classified from aerial photographs as "A", good quail range; "B", fair quail range; or "C", poor quail range, for both 1941 and 1950. Thirty-six coveys were present on the north Decatur Area in 1941 compared to twenty-four in 1950. No fundamental changes in the ratios of "A", "B", and "C" forties were

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<sup>1</sup>Doctoral thesis number 1804, submitted June 1, 1956. Chairman of Committee, E.L. Kozicky, Department of Zoology and Entomology.

<sup>2</sup>A.B., University of Arizona, Tucson. M.S., *ibid*.  
Graduate Assistant, Agricultural Experiment Station.

apparent from 1941 to 1950.

Forty-seven north Area forties which supported coveys in 1941 and/or 1950 were selected for detailed cover measurement and comparison. The cover type and land-use criteria used included crops, pasture, timber, homesteads, wasteland, and unclassified. The total acres of each cover type per forty, the average field size per forty, and linear feet of edge between the various types per forty were determined from the aerial photographs. The 1941 to 1950 comparisons of area and edge measurements were made for forties occupied in 1941; forties occupied in 1950; forties occupied in 1941 and 1950; forties occupied in 1941 but not in 1950; and forties occupied in 1950 but not in 1941. Although some minor changes in cover and edge relationships were found in the various forty combination comparisons, no fundamental changes in crop acreages, field sizes, or linear feet of edge per forty could be demonstrated that were believed to be of biological significance for bob-whites.

For comparative purposes daily whistle counts were obtained at two listening posts (Sections 11 and 13) from sunrise to two hours after sunrise. By separating whistling bob-whites as individuals during each five-minute interval, it was possible to compute call indices (mean number of birds heard whistling) for each one- to five-minute interval over the entire count.

The mean number, standard deviation, and coefficient of variation were computed for each one- to five-minute interval over the first and second hours after sunrise for the Sections 11 and 13 data for 1954 and 1955. In general, as the length of the interval increased the coefficient of variation decreased. The minor differences between the coefficients of variation of the three-, four-, and five-minute intervals indicated that the three-minute interval would provide the most information in a roadside whistle count of bob-whites.

The one- to five-minute call indices for twenty-seven days, separated into three nine-day periods, for the Sections 11 and 13 data for 1954 were subjected to analyses of variance. The components of variation examined were periods, days within periods, hours (first versus the second after sunrise), and the interaction periods times hours, and hours times days within periods. Periods were statistically significant in each analysis; this being ascribed to seasonal decline in whistling activity. Days within periods were also significant in each analysis, indicating considerable day to day variation in whistling within each period. Hours were significant for each of the analyses at Section 13, but only for the one-minute interval at Section 11. The interaction periods times hours was significant for the one- and two-minute analyses for Section 12. The interaction of hours times days within periods was significant in each of the analyses indicating greater whistling activity during the first hour than during the second, and vice versa for different days within a given period.

The influence of weather on whistling behavior was examined by correlating daily three-minute call indices with averages of wind velocity, temperature, vapor pressure deficit, absolute humidity, nebulosity, and dewfall obtained at the start and end of each count. Since the simple correlations did not account for the observed whistling variation, the independent and combined effects of wind, temperature, and vapor pressure deficit were examined by multiple regression analysis for the 1955 Sections 11 and 13 data. Weather accounted for only 35.4 per cent of daily whistling variation at Section 13. A highly significant value for temperature accounted for most of the variation. At Section 11, 13.1 per cent of whistling variation was due to weather, and none of the weather variables was significant. Multiple regression analysis of the pooled within Sections 11 and 13 data indicated that only 19.9 per cent of the variation in whistling was due to weather. A significant temperature value in the pooled analysis reflected the high value found at Section 13. The possibility that daily variation in call indices may have been confounded with seasonal trends in temperature, seasonal decline in whistling, and/or movements of birds away from the station is supported by two apparent levels of call indices at Section 13 but not at Section 11.



From twenty-seven records of individual bob-white whistling patterns during two-hour counts it was found that individuals whistled from thirty-one to 105 minutes during a two-hour count. Whistles per minute per bird ranged from one to nine with individual averages ranging from 4.2 to 1.8 whistles per minute over the entire two hour count. The number of moves by individual bob-whites during a count ranged from none to six with distances moved ranging from 100 to 800 feet.

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## CHELATE RING DERIVATIVES OF AZO DYES<sup>1</sup>

John LaVerne Ellingboe<sup>2</sup>

Department of Chemistry

A series of azo dyes was prepared to determine the type of structure needed for the formation of complexes with calcium and magnesium. The dyes selected were purposely simple in character to facilitate purification and to render unambiguous the interpretation of results. The dyes were all carefully purified and the majority of them were obtained in crystalline form. Absorption spectra of the dyes and of their calcium and magnesium complexes were obtained. Where complexes were formed, the nature of the complexes and their formation constants were determined.

Calcium and magnesium do not form complexes with azo dyes unless the dyes contain two groups ortho to the azo group. One of these groups must be a hydroxyl and the other either a carboxyl or a hydroxyl. With a *o*-carboxy-*o*'-hydroxyazo dye, the complex formed is two orders of magnitude weaker than the corresponding *o*,*o*'-dihydroxyazo dye. The complexes with the dyes and metals are all formed in the ratio of one to one with one exception; in the case of 1-(2-hydroxy-1-naphthylazo)-2-hydroxy-5-phenylbenzene a two to one complex is formed when the solution contains twenty per cent of acetone. This dye forms a one to one complex when no acetone is present.

When calcium or magnesium forms a complex with an azo dye, a change in the absorption spectrum of the dye results. In the case of the *o*,*o*'-dihydroxyazo dyes, the shift is towards shorter wave lengths; with the *o*-carboxy-*o*'-hydroxyazo dyes the shift is towards longer wave lengths.

This shift in absorbency is proportional to the strength of the complex formed. A plot of the log of the formation constant versus the absorbency shift yields a straight line for magnesium but shows rather poor correlation for calcium.

Most of the dyes that form complexes would be suitable as indicators for the titration of calcium and magnesium with ethylenediaminetetraacetic acid.

The combining ratios, formation constants, and ionization constants were determined spectrophotometrically in buffered solutions at constant ionic strength.

A new indicator for the titration of calcium with ethylenediaminetetraacetic acid in the presence of magnesium has been prepared by condensing iminodiacetic acid with fluorescein. In highly alkaline solution the indicator is brown and its calcium complex is a yellow-green. At lower pH values the free indicator is also a yellow-green. Magnesium does not form a complex with

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<sup>1</sup>Doctoral thesis number 1797, submitted May 31, 1956.

Chairman of Committee, Harvey Diehl, Department of Chemistry.

<sup>2</sup>B.A., St. Olaf College, Northfield, Minnesota. M.S., Iowa State College, Ames. Research Associate, Industrial Science Research Institute.

the indicator. The indicator may be used for the determination of calcium in water, limestone, or other calcium compounds.

To determine calcium directly using ethylenediaminetetraacetic acid as the titrant, the pH is made sufficiently high so that the magnesium is largely precipitated as the hydroxide. Owing to the high pH at which the titration is performed, some of the calcium is precipitated as the hydroxide at the beginning. Vigorous stirring is necessary to dissolve the hydroxide as the titration progresses. If the stirring is slow, false end points are obtained, the color returning after each change as the stirring is continued. The indicator is completely reversible.

Large amounts of sodium salts do not affect the titration. Strontium and barium interfere and are titrated along with the calcium. Copper and iron interfere with the end point, but such interference is easily obviated by the addition of cyanide.

Results are given for analyses on two limestone samples from the Bureau of Standards, two samples of limestone from the Standard Sample Co., Ames, Iowa, and a sample of selenite, obtained from the G. Frederick Smith Chemical Co., Columbus, Ohio.

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#### HOST-PARASITE RELATIONSHIPS OF ENDOCONIDIOPHORA FAGACEARUM BRETZ, THE CAUSE OF OAK WILT<sup>1</sup>

Arthur William Engelhard<sup>2</sup>

Department of Botany

Host-parasite relationships of Endoconidiophora fagacearum Bretz and susceptible oak hosts in northern Iowa were studied to determine: 1) if periods of host resistance occur during the year, 2) the symptoms as found in Iowa, 3) the factors affecting development of fungous mats and pads, 4) the association of host moisture and mat and pad development on red (Quercus spp.) and bur (Q. macrocarpa Michx.) oaks, 4) the possible role squirrels play in the dissemination of E. fagacearum, and 6) methods for controlling mat and pad formation.

Spring (dwarf-leaf) symptoms, previously undescribed, were found to be prevalent on infected red oaks in Pilot Knob State Park. Evident shortly after bud-break, trees displaying these symptoms showed small, pale green foliage and retarded leaf development.

Inoculation studies between February 1, 1953 and May 20, 1954, involving the use of laboratory-grown cultures, "ascospore-droplets" and fungous mat and pad material for inoculum indicated the latter is ineffective and ascospores are very effective. Trees inoculated between April 25 and August 28 with laboratory-grown cultures ("B" strain) became infected. Trees inoculated between October 3 and April 25 did not become infected regardless of type of inoculum used.

Wood moisture percentages (oven dry weight) were determined on red and bur oaks under mats, under pads, in orange-brown odoriferous wood 2 to 6 inches from mats and pads and, when present, in streaks of "green" wood occurring near mats and pads. Two one-inch cores of wood were taken with

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<sup>1</sup>Doctoral thesis number 1717, submitted August 20, 1955.

Chairman of Committee, W.H. Bragonier, Department of Botany.

<sup>2</sup>B.S., Ohio University, Athens. M.S., Yale University, New Haven, Connecticut. Graduate Assistant, Agricultural Experiment Station.

an increment borer for each sample. Each core was divided into a 3/8-inch sapwood section and a 5/8-inch outer heartwood section. The average moisture percentage of red oak sapwood under mats and pads formed in the spring of 1954 was 81 per cent (extremes 66 and 105); fall of 1954, 101 per cent (extremes 83 and 117); and spring of 1955, 84 per cent (extremes 74 and 103). The average moisture percentage of sapwood under three mats and pads on one bur oak in the spring of 1954 was 71 per cent (extremes 67 and 76), and in the spring of 1955, under three mats and pads on two bur oaks, 71 per cent (extremes 67 and 75). There was no appreciable difference between percentage moisture under mats and under pads on either bur or red oaks. The moisture percentage of orange-brown odoriferous sapwood 2 to 6 inches from mats and pads was similar to that under the mats and pads. The average sapwood moisture under mats and pads was 17 per cent higher on red oaks forming mats and pads in the fall than in the spring.

Seventy-two per cent of trees dead three or more years had over 50 per cent of the bark attached to the merchantable parts of the boles and seventy per cent had decay in the sapwood and the outer heartwood. Wood moisture of trees retaining the bark usually remained above 80 per cent, a level favoring decay. Trees from which the bark fell or was removed dried to a moisture content below the fiber saturation point and no visible decay was observed for a period of three years after death.

To study the influence of temperature on the formation of mats and pads of *E. fagacearum*, alternate 5-foot logs from eight trees were stored at 43°F, 55°F, 69°F, and 90°F. Mats and pads developed on all logs except those stored at 90°F. All the control logs stored in the woods formed mats and pads. Other evidence indicated high temperatures are responsible for the general lack of mat and pad development in the summer on trees otherwise in a condition to form mats and pads.

The frequency of mat and pad development on wilt-killed red oaks was observed during 1952, 1953, and 1954. At Pilot Knob State Park all 33 trees observed in 1952, 156 in 1953, and 37 in 1954 formed mats and pads with bark cracks over them. At Dolliver State Park, 18 of 20 trees formed mats and pads and bark cracks in 1953.

Evidence of squirrel feeding on mats and pads was observed at Pilot Knob State Park on 22 of 31 trees in 1952, 134 of 145 in 1953, and 21 of 23 in 1954. A female gray squirrel (*Sciurus carolinensis* Gmelin) observed feeding on a mat and pad on May 6, 1955, was collected; isolations made from both the mouth and stomach of the squirrel yielded *E. fagacearum*. Squirrel feeding on mats and pads correlated positively with periods when squirrels fed heavily on buds and expanding shoots. At Dolliver State Park squirrel feeding occurred on only one of 18 trees observed in 1953 and none on 20 trees in 1954.

Experiments to control mat and pad formation were carried out at Pilot Knob State Park on 90 red oaks. Treatments included 1) an 8-inch dry girdle at a height of approximately 4 feet, 2) a girdle painted three times with 40 per cent sodium arsenite, 3) a continuous frill to a height of 5 feet, and 4) bark painted to a height of 5 feet with 40 per cent sodium arsenite. Treatments were applied July 12 to trees wilting prior to July 1, and August 12 and 21 to trees, some of which wilted prior to and others after July 1. All treatments, regardless of when applied, reduced the number of mats and pads formed. Those applied July 12 were more effective in controlling mat and pad development than those applied August 12 and 21. The dry girdle was the most effective treatment, followed closely by the girdle plus sodium arsenite and the frill. No fungous development occurred above the girdle on any of the ten trees treated July 12; a small amount of fungous growth was observed in the difficult-to-control area between the girdle and the ground. There was no fungous growth in the treated areas on any of the 20 trees frilled to a height of 5 feet. A combination girdle and frill is suggested for use in attempting to control mat and pad growth on wilt-killed trees. Alternative suggestions are to use a single girdle near the ground or one near the ground and another at 4 or 5 feet.

# ESTIMATES OF GENETIC PARAMETERS INFLUENCING BLOOD SPOTS AND OTHER ECONOMIC TRAITS OF THE FOWL<sup>1</sup>

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This study was concerned with the inheritance of blood spots, rate of annual egg production, March egg weight, and age at sexual maturity. The purpose of the study was to determine the extent to which genetic and environmental factors influence these traits.

Blood spot measurements obtained by candling approximately 450,000 eggs from 22,245 White Leghorn hens over an eight year period were studied. Records from 17,356 White Leghorn hens were analyzed in the study of sexual maturity, egg weight, and egg production.

The hierarchical type of analysis of variance and covariance was the principal statistical method used to analyze the records. The data were analyzed by hatches, by sires within hatches, by dams within sires, and between full sibs from which variance and covariance components were obtained. These components of variance and covariance were used to estimate heritability, phenotypic and genetic correlations.

Hatch effects were small with regard to blood spots and March egg weight, but were more important for sexual maturity and annual egg production.

The heritability of blood spots was estimated to be 32 per cent when the incidence of blood spots is between one per cent and three per cent with an average sample size of 20 eggs.

Estimates of heritability of individual differences in annual egg production, age at sexual maturity and egg weight were obtained. A method for obtaining standard errors of heritability estimates based on unequal subclass numbers was investigated. The following estimates of heritability with their 95 per cent confidence limits were obtained:

<u>Trait</u>	<u>Heritability</u>	<u>Confidence Limit</u>
Egg production	34.8%	31.2 - 38.4
Sexual maturity	39.8%	36.2 - 43.4
Egg weight	51.4%	47.3 - 55.5

The following phenotypic correlations were obtained; averaged over the eight years' data:

<u>Trait</u>	<u>Phenotypic Correlations</u>	<u>Genetic Correlations</u>
Blood spots x egg production	+ .035	+ .082
Blood spots x sexual maturity	+ .020	-.096
Blood spots x egg weight	+ .002	-.044
Egg production x sexual maturity	-.404	-.548
Egg production x egg weight	-.002	-.113
Sexual maturity x egg weight	-.016	-.129

<sup>1</sup>Doctoral thesis number 1762, submitted February 8, 1956. Chairman of Committee, A. W. Nordskog, Department of Poultry Husbandry.

<sup>2</sup>B.S., Oklahoma Agricultural and Mechanical College, Stillwater.  
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Graduate Assistant, Agricultural Experiment Station.



All phenotypic correlations between the four traits were essentially zero with the exception of annual production x sexual maturity indicating that on a phenotypic basis early maturing birds lay more eggs to 72 weeks of age.

The genetic correlations indicate that birds which produce the largest number of eggs and mature earliest produce eggs having a higher incidence of blood spots. Also, birds having the highest rate of lay would tend to lay smaller eggs. Early maturing birds would have on the average a heavier egg weight and would tend to lay at a higher rate.

Finally, the estimates of heritability, phenotypic and genetic correlations, were used to construct selection indices which would maximize genetic improvement obtained from selection.

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### OBSTACLES IN PARTICIPATION IN THE IOWA SOIL CONSERVATION DISTRICTS PROGRAM<sup>1</sup>

Loyd K. Fischer<sup>2</sup>

Department of Economics and Sociology

The objectives of this study were 1) to ascertain and analyze the principal obstacles and resistances which have impeded the progress of the Iowa Soil Conservation Districts Program, and 2) to discover and develop means for the removal or mitigation of these obstacles and resistances.

The objective of the Districts Program for each farm was considered to be the application of the land-use practices recommended in the conservation plan for that farm. The land-use practices applied by the farmers on each field of tillable land were compared with practices recommended in the farm plans. The application on a given field of the practices recommended was considered to be the attainment of the objectives of the district for that field.

This investigation attempted to discover a) why some farmers participate in the Districts Program while others do not and b) of those farmers who do participate, to the extent of initiating farm plans, why some achieve the Program objective of erosion control while others fail to apply recommended land-use practices. Factors existing both on and off Iowa farms were identified as affecting farmer participation in the Program, as follows:

1. Certain characteristics of farm firms tend to impede the acceptance of farm plans, and compliance with district land-use recommendations.
2. Certain beliefs, customs, and habits of farm operators tend to make them resist applying conservation measures.
3. Certain administrative aspects of the Districts Program do not adequately facilitate progress toward Program objectives.

In this study the testing of obstacles hypothesized to exist on the farms was performed in two ways, as follows: 1) the procurement and analysis of data relative to specified farm characteristics for the purpose of investigating the possibility of correlation between such characteristics and the extent of compliance with district objectives within such farms, and 2) an inquiry into the

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<sup>1</sup>Doctoral thesis number 1741, submitted December 6, 1955. Chairman of Committee, John F. Timmons, Department of Economics and Sociology.

<sup>2</sup>B.Sc., University of Nebraska, Lincoln. M.S., *ibid*. Associate, Agricultural Experiment Station.

stated reasons of farm operators for complying or failing to comply with district recommendations. Samples of farms were drawn from among those which had not previously been planned by the district and from among farms having district plans. The population of cooperating farms was stratified into three categories according to the extent of compliance with district recommendations and a random sample was drawn from each stratum. Information about each farm was obtained by personal interviews with the farm operators.

In the investigation of characteristics of farm firms various factors were analyzed in terms of their effect on farmers' acceptance of district plans, and application of recommended conservation treatments. Chi-square tests of interdependence of the data obtained indicated that district progress was impeded significantly by small size of farm; tenant operatorship; cash and crop-share leasing arrangements; and high inherent productivity of the land.

From the investigation of reasons expressed by farm operators for not complying with district recommendations, two stand out as the most important. In general, farmers who had not accepted recommendations believe that their present land-use practices would adequately conserve soil resources, and that the suggested conservation measures were uneconomic. Conversely, farm operators who had applied given conservation measures had done so because they felt morally obligated to maintain soil productivity, and that the conservation measures could be profitably applied.

The major part of the empirical analysis of this study was concerned with the identification of on-the-farm impediments to districts' progress. The primary objective of this study, however, is to devise means whereby the Districts Program might be improved. Therefore, the Program has been analyzed in light of on-the-farm obstacles indicated above, and suggested principles of public administration. Adjustments necessary to correct hypothetical weaknesses in the Districts Program are suggested, as follow:

1. What the Districts Program is expected, or is attempting, to accomplish should be clearly established by law or by administrative decision.
2. A system of priority or precedence should be assigned the various objectives of the Program according to their urgency and/or the extent of public interest therein.
3. To serve as guides for allocating resources and for directing the efforts of district personnel, methods of evaluating district accomplishments should reveal the actual progress being made toward Program objectives.
4. In order to maximize progress, within the limits of the resources available, toward the specified objectives of the Districts Program, criteria must be carefully developed to guide the allocation of the Program's resources:
  - a. Between the various districts.
  - b. Between farms within districts.
  - c. Between practices within farms.
  - d. Between the various aspects of the Districts Program (e.g., educational and promotional efforts and technical assistance; maintenance of old plans and writing of new ones).
5. The Districts Program should be coordinated with the programs of other public and private organizations having related goals so that the various activities do not conflict but rather complement each other.

6. The Districts Program should have resources to provide aid and incentive sufficient to induce individuals to use recommended erosion-control practices; and/or power to require certain minimum standards of land-use.
7. The objectives and operating procedures of the Districts Program should be constantly reviewed and adjusted in the light of the dynamic environment in which the Program operates.

Strong features of the Districts Program and characteristics common to those farm firms which have attained specified district objectives provide the foundations for further progress. Conversely, weak features of the Districts Program and characteristics common to farm firms which have failed to attain specified district objectives suggest adjustments in the interest of furthering progress toward objectives of soil conservation.

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#### THE SEPARATION OF SOME INORGANIC COMPOUNDS BY LIQUID-LIQUID EXTRACTION<sup>1</sup>

Raymond A. Foos<sup>2</sup>

Department of Chemistry

The use of liquid-liquid extraction for the separation of some inorganic compounds was demonstrated in this study. The separations included tantalum from niobium, tantalum from vanadium, zirconium from hafnium, and yttrium from some rare earths. Tantalum and niobium spectrographically free of each other and hafnium spectrographically free of zirconium were prepared in quantity on a continuous basis. High purity fractions of zirconium, yttrium, and vanadium were also prepared while the rare earths were divided into enriched fractions.

Many single and multistage extractions employing immiscible organic solvents were carried out on aqueous solutions of the compounds to be separated. Analyses of the equilibrium phases allowed calculation of individual distribution coefficients and their separation factors. Single stage extractions were employed to obtain data from which the operation conditions for the multistage countercurrent extractions were estimated.

A tantalum-niobium mixture which contained about equal weights of each was obtained by processing a columbite-tantalite ore. An aqueous solution, or stock solution, containing the equivalent of 517 grams of tantalum and niobium pentoxides per liter was prepared by dissolving the hydrated oxides in excess hydrofluoric acid. Single stage extractions of this stock solution or its water dilutions with many organic solvents indicated that some solvents extracted more than 50 per cent of the total tantalum analyzing less than one per cent niobium. Although the ketones were most effective for obtaining this separation, many alcohols, amines, aldehydes, ethers, esters, organic phosphates, organic phosphites, and mixed organic solvents were also useful. A multiple-contact batch extraction of the diluted stock solution carried out with diethyl ketone gave in three stages a 99 per cent recovery of niobium spectro-

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<sup>1</sup>Doctoral thesis number 1567, submitted June 18, 1954.

Chairman of Committee, Harley A. Wilhelm, Department of Chemistry.

<sup>2</sup>B.S., Xavier University, Cincinnati, Ohio, 1950. M.S., *ibid.*, 1953.

Research Assistant, Institute for Atomic Research.

graphically free of tantalum and a 96 per cent recovery of the tantalum which analyzed about 0.15 per cent niobium. The most effective separation of tantalum from niobium was obtained when the free hydrofluoric acid content was low.

Other less corrosive systems were investigated for separating tantalum from niobium by liquid-liquid extraction. Extraction of hydrofluoric acid solutions of niobium and tantalum which had been partially or completely neutralized with aliphatic or aromatic hydroxyamines indicated favorable mass distribution and separation of tantalum from niobium. Tantalum preferred the organic phase in these systems. Although the same general extraction trends were observed for the amine-free and the amine-neutralized hydrofluoric acid solutions of niobium and tantalum, the former system gave higher degrees of separations. Niobium was preferentially extracted by the organic phase from a potassium hydroxide solution of niobium and tantalum. However, in this system the mass transfer and degree of separation was low.

Several countercurrent multistage extractions were carried out in which diethyl ketone was employed as the organic phase and the amine-neutralized hydrofluoric acid solution of niobium and tantalum as the aqueous feed. In from 10 to 15 stages tantalum and niobium spectrographically free of each other were obtained quantitatively on a continuous basis.

Tantalum and vanadium pentoxides, in about equal weights, were dissolved in hydrofluoric acid and then extracted by several organic solvents. From a single stage extraction with tributyl phosphate greater than 90 per cent of the tantalum analyzing less than 2.0 per cent vanadium was recovered from the equilibrium organic phase. These inorganic compounds could probably be quantitatively separated by liquid-liquid extraction in three or four stages.

A mixture composed of about 97 per cent hafnium and about three per cent zirconium as oxychlorides was dissolved in nitric acid. Extractions of this aqueous solution showed that zirconium was preferentially extracted by tributyl phosphate. The presence of nitric acid increased mass transfers to the organic phase but decreased the hafnium-zirconium separation factors. A pilot plant continuous operation employing a 17 stage countercurrent extractor yielded 90 per cent of the hafnium spectrographically free of zirconium.

The yttrium-rare earth concentrates were obtained from Fergusonite ore, Gadolinite ore and a by-product from an ion-exchange resin separation process. In each case the mixture in terms of oxide was composed of from 50 to 60 per cent yttrium and 5 to 15 per cent heavy rare earths with the light rare earth fraction constituting the remaining material. Tributyl phosphate was generally employed for extracting nitric acid solutions of these concentrates.

Single stage extractions indicated that the relative extractability of certain rare earths from an aqueous system 3.0 molar or greater in nitric acid increases with atomic number. At lower nitric acid concentrations deviations from this trend were observed. The mass transfer values showed a minimum at a nitric acid concentration of about 6.0 molar. Yttrium extracts in the holmium region from a highly concentrated nitric acid system, in the dysprosium region from a 6 to 12 molar nitric acid system, in the gadolinium region from a 3.0 to 4.5 molar nitric acid system and with the lighter rare earths from very low nitric acid systems.

A number of 20 stage countercurrent extractions were carried out employing nitric acid solutions of yttrium and rare earths as the aqueous feed phase and tributyl phosphate as the organic phase. When extracting their concentrated nitric acid solutions, the organic product generally contained yttrium and heavy rare earths while the aqueous product contained the light rare earth fraction plus a small amount of yttrium and dysprosium. In one multistage extraction the organic product phase delivered 90 per cent of the total yttrium which gave an oxide that was 91 per cent pure. Extraction of a light rare earth fraction resulted in an enriched concentrate of praseodymium and samarium. Gadolinium and dysprosium were separated from yttrium to a considerable



extent by extracting from a very low nitric acid solution. The extractions of these yttrium-rare earth concentrates showed the possibility of separating yttrium from any particular rare earth and of some individual rare earths.

The liquid-liquid systems presented here indicated further the applicability of solvent extraction for separating inorganic compounds. Much of the information from this work is directly applicable to practical separation problems and therefore should be readily adaptable to specific laboratory and industrial scale operations.

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### UNIVERSAL SWING CURVES FOR TWO-MACHINE STABILITY PROBLEM WITH MULTIPLE SWITCHING<sup>1</sup>

Abdel-Aziz Ahmed Fouad<sup>2</sup>

Department of Electrical Engineering

The purpose of a transient stability study of an electrical power system is to determine whether synchronism between the synchronous machines will be maintained after the occurrence of some transient disturbance.

For a stable two-machine power system, the phase angle  $\delta$  between the emfs of the two machines must not increase indefinitely with time after the transient occurs. Thus, a transient stability study seeks a relation between the angle  $\delta$  and time, and examines this relation to determine the behavior of the angle  $\delta$  after the occurrence of the transient. This relation is called the swing equation.

In this dissertation, general precalculated solutions of the swing equation are presented. The solutions were developed for a system of one machine against an infinite bus, but they can be used for any two-machine system, since the latter can be reduced to an equivalent system similar to the former.

The solutions were obtained by solving the swing equation by a step-by-step incremental calculus process, using the Network Analyzer of Iowa State College.

The swing equation is a second order differential equation, and its solution depends on the parameter  $p$  of the system and the initial conditions. The parameter  $p$  of the system depends on the amplitude of the power-angle curve, the initial power delivered by the equivalent finite machine, and a constant depending on the network between the finite machine and the infinite bus. The initial conditions are the initial angle  $\delta_0$  and the initial angular velocity  $\omega_0$ .

Solutions for different values of  $\sin \delta_0$ ,  $\omega_0$ , and  $p$  are presented in the form of curves. The curves are plots of the angle  $\delta'$  and the velocity  $\omega$  against modified time  $\tau$ , where  $\delta'$  differs from the angle  $\delta$  by a constant depending on the network between the machines and  $\tau$  is related to the actual time by a factor that depends on the system under consideration.

To solve a two-machine transient stability problem with the aid of these curves the following steps are taken:

1. The system is reduced to an equivalent one machine against an infinite bus.
2. The values of  $p$  and  $\tau$  are then calculated for the condition immediately following the occurrence of the transient. Knowing  $p$ ,  $\delta_0$ , and  $\omega_0$ , the proper precalculated solution is selected.

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<sup>1</sup>Doctoral thesis number 1802, submitted June 1, 1956.

Chairman of Committee, W.B. Boast, Department of Electrical Engineering.

<sup>2</sup>B.Sc., Fouad University, Egypt. M.S., State University of Iowa, Iowa City.

3. If the network is changed, a new value of  $p$  prevails. Thus, a new precalculated solution is to be followed. At that instant of switching, the angle  $\delta$  and the velocity  $\omega$  are determined from the previously selected curves, from which  $\delta_0$  and  $\omega_0$  for the new solution are obtained.
4. This process can be repeated for as many switching processes as required.

The solutions presented apply for any two-machine system with a general impedance network, and for multiple switching procedures. Their accuracy is comparable to the analytical step-by-step solutions usually used, with the advantage of minimum calculations and great saving in time involved.

The approximations used in developing the curves are the ones usually made in transient stability studies, mainly that the machines are represented by constant emfs behind transient reactances, and damping torques are neglected.

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## KINETICS OF HERBICIDAL ACTION<sup>1</sup>

Robert E. Frans<sup>2</sup>

Department of Botany

A considerable amount of work has been done on the basic mechanisms of plant growth, and particularly on the mechanism of action of applied and endogenous auxins. Increased knowledge concerning such processes has aided in determining commercial usages of synthetic auxins, notably in the herbicidal field. There is little quantitative evidence available, however, that can be used to interpret satisfactorily the mechanism of growth inhibition in plants. This investigation represents an attempt to relate inhibition to molecular reactions within the plant by means of a kinetic analysis. It is proposed that an herbicide or growth substance (H) combines reversibly with some mechanism or site (M) within the plant cell to form a herbicide-mechanism complex (HM). This complex is then thought to be transformed irreversibly into products which ultimately give rise to growth inhibition. These reactions are expressed as follows:



Soybean seedlings were treated at the primary leaf stage with a number of compounds at concentrations necessary to cover completely the inhibitory range. Growth was measured as the increase of fresh weight of all plant material above the primary leaves 10 to 14 days after treatment. Plots of percentage inhibition of growth against concentration of chemical resulted in hyperbolas which were transformed satisfactorily to straight lines by plotting the reciprocal of percentage inhibition rate against the reciprocal of concentration. The hyperbolic inhibition curves are described by the Michaelis-Menten equation

<sup>1</sup>Doctoral thesis number 1697, submitted July 12, 1955.

Chairman of Committee, W.E. Loomis, Department of Botany.

<sup>2</sup>B.Sc., University of Nebraska, Lincoln. M.S., Rutgers University, New Brunswick, New Jersey. Associate, Agricultural Experiment Station.

$$v = \frac{V_{\max} (H)}{K_m + (H)}$$

which was developed to describe enzyme systems, and later modified to include auxin-induced growth. The straight line plots of the data are derived by taking the reciprocal of the initial velocity equation, and providing a means of determining values for the maximum velocity constant ( $V_{\max}$ ) and the dissociation constant ( $K_m$ ) of the reversible reaction.

Growth inhibition of soybean seedlings induced by single applications of 2,4-dichlorophenoxyacetic acid (2,4-D), 2,2-dichloropropionic acid, 2,4,5-trichlorophenoxyacetic acid (2,4,5-T), trichloroacetic acid, 3-amino-1,2,4-triazole, indole-3-acetic acid (IAA), and maleic hydrazide (MH), satisfactorily supported the hypothesis inherent in the kinetic analysis. It was found that the calculated dissociation constant ( $K_m$ ) of the reversible reaction may be of value in determining relative affinities of these compounds for sites or mechanisms within the plant.

Experiments with yeast cultures were initiated to avoid certain of the obvious sources of variability inherent in greenhouse experiments. Results obtained by single additions of 2,4-D, coumarin, and IAA to yeast cultures showed satisfactory agreement to straight line reciprocal plots, and between calculated and experimental percentage inhibition. The calculated constants were of little value, however, in characterizing or comparing compounds, since the calculated maximum velocities obtained for 2,4-D, coumarin and 2,4,5-T were in excess of the possible 100 per cent. Results obtained with 2,4,5-T were not satisfactorily interpreted by this analysis.

The kinetic analysis was extended to responses obtained from combinations of growth substances in an attempt to understand more clearly the nature of their interactions in producing growth inhibition. It was found that growth inhibitions of soybean seedlings induced by low concentrations of 2,4-D was competitively inhibited by 2,4,5-T and IAA. The competitive action was not evident at higher concentrations of 2,4-D. The effect of 2,3,5-triodobenzoic acid (TIBA) and MH was to increase, apparently additively, inhibition caused by 2,4-D and IAA. It was suggested that any competitive effects that might have existed were largely masked by the stronger inhibitive effects of the secondary compound (TIBA and MH) on an inhibitory site separate from that of the primary compound (2,4-D or IAA).

Growth inhibition of yeast cultures induced by 2,4-D was found to be increased additively by 2,4,5-T, coumarin, and IAA, and synergistically by TIBA. The apparently contradictory results obtained with 2,4,5-T and IAA in combination with 2,4-D in yeast and soybean experiments, are thought to be a function of possible differential utilization of growth substances by yeast.

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I. DIRECT TITRATION OF SULFATE  
II. HIGH PRECISION SPECTROPHOTOMETRIC ANALYSIS<sup>1</sup>

Max Q. Freeland<sup>2</sup>

Department of Chemistry

A method is proposed in which sulfate is titrated directly with standard barium solution. The end point is indicated by the adsorption of Alizarin Red S or Thorin onto the barium sulfate with a distinct color change from yellow to pink. The sulfate sample must contain 30 to 40 per cent methanol for these indicators. Coprecipitation errors are greater than for gravimetric sulfate methods, but most of these can be avoided by the preliminary removal of cations with an ion exchange column. In the absence of interfering anions the ion exchange titrimetric method is as precise as the gravimetric method and considerably faster.

A complete review of literature on titrimetric sulfate determination is included with bibliography. The experimental work leading to the proposed method is detailed and discussed.

Optically matched cuvettes are necessary for existing high precision spectrophotometric methods. The maintenance of optical matching is not practical for routine analysis at high precision. Procedures are presented utilizing a modification of the Beer's law equation which permit the use of unmatched cuvettes for high precision spectrophotometric analysis. The errors brought about by the use of unmatched cuvettes are calculated and they indicate the optimum conditions, relative to mismatching, for the use of the existing methods.

These procedures were applied to the analysis for vanadium in three vanadium-aluminum alloys. The accuracy obtained on synthetic samples averaged 0.1 per cent. The reproducibility on the actual samples averaged better than 0.2 per cent.

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<sup>1</sup>Doctoral thesis number 1684, submitted June 17, 1955.

Chairman of Committee, James S. Fritz, Department of Chemistry.

<sup>2</sup>B.S., Northeast Missouri State Teachers College, Kirksville, M.S., Iowa State College, Ames. Research Assistant, Institute for Atomic Research.

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ADHESION BETWEEN BITUMENS AND AGGREGATES<sup>1</sup>

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Department of Civil Engineering

The service life or durability of bituminous pavements depends greatly on the adhesion quality between bitumens and aggregates. Some aggregates by nature have greater affinity with water than bitumens. As a result, large percentage of failure is caused by the separation of the bitumen films from the wet aggregate surfaces. Even in dry aggregates, satisfactory adhesion can only be achieved through the proper control of viscosity and temperature of the bitumens.

Adhesion between bitumen binders and aggregates is a surface phenomenon.

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<sup>1</sup>Doctoral thesis number 1810, submitted June 4, 1956.

Chairman of Committee, Ladis H. Csanyi, Department of Civil Engineering.

<sup>2</sup>B.Sc., Lingnan University, China. M.S., Iowa State College, Ames.

The degree of adhesion is dependent upon the wetting ability of the bitumen and its mutual affinity with the aggregate surface. Factors affecting this phenomenon are numerous. In this investigation, emphasis was centered mainly on the variations in viscosity and surface tension of different bitumens and the surface characteristics of the aggregates that may affect the binding quality. By measuring the angles of contact in the interfaces of bitumens and aggregates, the degree of adhesion affected by any of these factors can be evaluated.

Thirty bitumens with the range of 30-300 penetrations were selected from three different sources. Rheologically, they are all of non-Newtonian flow characters at temperatures below 200°F. In the high temperature range, they tend to lose their plastic flow and approximate to simple liquid. The relationship between viscosity and temperature in the log-log plots generally gave the straight line variations within the temperature range 140 to 400°F. Such relationship can be expressed by the empirical formula:

$$\log \eta = k T_{\text{abs}}^{-m}$$

where  $\eta$  is the absolute viscosity in centipoise,  $T_{\text{abs}}$  is the absolute temperature in Rankine,  $k$  and  $m$  are constants. The over-all advantage of this equation is that it furnishes a convenient means of predicting viscosity of all kinds of bitumens at temperatures within the range of 140 to 400°F and the exponent  $m$  is useful for measuring the temperature susceptibility of bitumens.

Results indicated that bitumens of equal penetration do not necessarily have the same viscosity or equal angle of contact under the same temperature. Therefore, the general practice of using penetration alone to determine the properties of bitumens is fallible.

The relationship between surface tension and temperature is also found to be in linear function. Abrupt transitions in the surface tension-temperature curves indicated that the change of states from semi-solid to liquid took place at the temperature range of 200 to 250°F. In the highly aromatic cracked bitumens, the points of transition occurred at a lower temperature than that of the aliphatic bitumens.

To study the degree of adhesion between bitumens and aggregates, small bitumen droplets of known viscosity were deposited on smooth glass or polished and split aggregate surfaces. The angles of contact were measured under the microscopes either with the aid of the protractor eye-piece or by computation of the measured dimension of the droplet segment. The advantage of using smooth glass surfaces is to eliminate all effects due to roughness, absorption, and polarity in natural aggregates. Thus the data obtained will furnish information concerning the effects produced by the bitumens alone.

The technique for determining contact angles formed on aggregate surfaces is theoretically sound and useful. The small drop of bitumen can be applied successfully to the small area of the irregular surface which assumed the advancing angle of contact. Two types of aggregates, the hydrophobic limestone and the highly hydrophilic Black Traps were used. Contact angles formed on the Black Trap aggregates were generally larger than those on limestone surfaces. This result is well correlated with the findings performed on the chemically treated glass surfaces and approximated to the general belief that acidic aggregates gave poorer adhesion with bituminous paving materials. On split and polished surfaces of both aggregates, differences in contact angles among bitumens of similar penetration at a temperature above 250°F is not great, whereas below that temperature, smaller angles were formed on the polished aggregate surfaces than on the split surfaces. Comparison between the degree of roughness and the petrological nature of aggregates to adhesion show that the former exerts greater influence than the latter. Finally, when no external forces are influencing the droplet, the equilibrium angle of contact once formed did not alter. This indicates that initial wetting will decide adhesion tension between bitumens and aggregates.



EFFECTS OF VARYING PROTEIN AND ENERGY VALUE OF DIETS  
ON NITROGEN UTILIZATION AND BODY COMPOSITION  
OF ADULT FEMALE RATS<sup>1</sup>

Pilar A. Garcia<sup>2</sup>

Department of Food and Nutrition

The present study attempts to relate varying intakes of dietary protein and food energy to nitrogen utilization and body composition of adult female albino rats.

Groups of animals were given different amounts of protein as lactalbumin during ad libitum feeding. This was followed by a period of caloric restriction to two-thirds of the ad libitum intake and accompanied by the same, or more, or less protein than consumed voluntarily. In five experiments information was obtained about nitrogen balance, carcass and liver nitrogen, body fat and hemoglobin concentration in the blood. Xanthine oxidase, succinic dehydrogenase and cytochrome oxidase systems in liver tissues were also studied. Daily records of food consumption and body weights were kept.

In the first experiment, diets supplying 15, 10, or 5 per cent of the calories as protein were fed ad libitum to 3 groups of rats. At these three intakes of protein, the daily nitrogen intake per rat was equivalent to approximately 200, 140, or 70 mg. When nitrogen equilibrium was achieved, the food intakes of the animals in each group were reduced to two-thirds of that consumed voluntarily without altering the absolute amount of protein. Feeding was continued until nitrogen equilibrium was re-attained. In the succeeding 4 experiments, diets supplying 15 or 5 per cent of the calories as protein were fed ad libitum to two groups of animals for 20 days. Then each group of rats was divided into 3 subgroups. For the next 30 days, subgroups A, B, and C which were pre-fed 15 per cent of their calories as protein received the same, two-thirds or one-third as much protein in diets supplying two-thirds as much food energy. Subgroups D, E, and F which were pre-fed 5 per cent of their calories as protein received three times, twice, or the same amount of protein in diets supplying two-thirds as much food energy. Subgroups A and D, B and E, and C and F consumed approximately the same amounts of nitrogen.

Stock animals were sacrificed at the beginning of the last 3 experiments to serve as controls. At the end of ad libitum feeding, animals representing each group were also sacrificed.

Nitrogen retention increased with increments in protein intake when food consumption was unrestricted. On the other hand, animals fed the higher protein diet voluntarily consumed less food than those fed the lower protein diet. After caloric restriction was imposed, nitrogen losses occurred regardless of the intake of protein. Rats in subgroups D and E were in nitrogen equilibrium or retained nitrogen during the first 5 days of restricted feeding, however. Nitrogen equilibrium was re-attained by all the animals by the end of 30 to 35 days of caloric restriction. With similar nitrogen intakes after restriction of food, higher nitrogen losses occurred in animals pre-fed 15 per cent of their calories as protein than in those pre-fed 5 per cent of their calories as protein. On the other hand, if the same amount of nitrogen was fed during both ad libitum and restricted feeding, caloric restrictions determined nitrogen loss.

<sup>1</sup>Doctoral thesis number 1709, submitted August 11, 1955. Chairman of Committee, Charlotte E. Roderuck, Department of Food and Nutrition.

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Graduate Assistant, Agricultural Experiment Station.

Weight gains during ad libitum feeding and weight losses during restricted feeding were related to nitrogen balance but not to the intake of either food energy or protein.

The liver weights of stock control and ad libitum-fed animals did not differ significantly. Considerable reduction in liver weights, accompanied by a decrease in their total nitrogen content and an increase in their percentage of protein, occurred at the end of caloric restriction. A significant relationship existed between the percentage of liver protein and the average daily caloric intake per 100-gram rat. Although total liver nitrogen was directly related to protein intake during ad libitum feeding, no such relationship existed after restriction of food energy. The percentage of liver protein was related to the intake of protein during either ad libitum or restricted feeding, and after caloric restriction it was independent of the previous protein intake.

Unit activities of both xanthine oxidase and succinic dehydrogenase in liver tissues were related directly to the protein concentration of the liver. During ad libitum feeding, unit activities of these enzymes were also related linearly to protein intake. Following restriction of food intake, their unit activities had increased. At the same time, unit activities of xanthine oxidase had also been raised significantly by increments in protein intake but had not been lowered significantly by decrements. Unit activities of succinic dehydrogenase during the period of restricted feeding decreased significantly with successive decreases in protein intake and increased with increments in protein intake.

During ad libitum feeding, total activities of xanthine oxidase and succinic dehydrogenase were related directly to protein intake. After caloric restriction, the total activities of these enzymes were lower than before, except in livers of rats fed increased amounts of protein.

Caloric restriction appeared to increase the unit activity of cytochrome oxidase. At the same time, increments in protein intake seemed to increase the unit activity of this enzyme while decrements had no effect. Total activities of cytochrome oxidase appeared to be lower after caloric restriction than during ad libitum feeding.

Data obtained on body fat were variable and no significant relationships with changes in dietary intake of either protein or calories were observed, although animals pre-fed 5 per cent of their calories as protein tended to be fatter after 30 days of restricted feeding than those pre-fed 15 per cent of their calories as protein.

Neither the concentration of nitrogen in the carcasses nor the hemoglobin concentration in the blood of rats after caloric restriction was significantly influenced by the intake of protein during restricted feeding.

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THE PREPARATION AND CLEAVAGE OF SOME  
ORGANOGERMANIUM COMPOUNDS<sup>1</sup>Clare William Gerow<sup>2</sup>

Department of Chemistry

The physical and chemical properties of organogermanes were compared with organosilanes and the literature of organogermanes was reviewed from 1950 until January, 1956. Groups of tables were compiled which contain the physical properties of all organogermanes appearing in the literature from 1950 until January, 1956.

Triphenylgermylpotassium was prepared by the cleavage of tetraphenylgermane by sodium-potassium alloy in both diethyl ether and ethylene glycol dimethyl ether, and by the cleavage of hexaphenyldigermane with sodium-potassium alloy in diethyl ether in the presence of either tetrahydrofuran or bromobenzene. Triphenylgermyllithium was prepared in about 70 per cent yield in ethylene glycol dimethyl ether by the cleavage of tetraphenylgermane, hexaphenyldigermane and triphenylchlorogermane with lithium. Triphenylgermyllithium was also prepared by the reactions of methylithium, *n*-butyllithium and phenyllithium with triphenylgermane. Diphenyl-2-phenylethylgermyllithium was prepared by the cleavage of diphenyl-bis-(2-phenylethyl)germane with lithium in ethylene glycol dimethyl ether. Attempts to prepare trialkylgermyllithium compounds by analogous procedures were unsuccessful.

Triphenylgermyllithium was found to react with alkyl halides but not with aryl halides, with certain olefins, with some compounds containing azomethine and azo linkages, with 1,2-epoxides, with fluorene and with bromine. With 1,1-diphenylethylene there was obtained triphenyl-(2,2-diphenylethyl)-germane, m.p. 99-100° and with octadecene-1 there was obtained triphenyl-*n*-octadecylgermane, m.p. 76-77°, thus indicating a high degree of reactivity for this type of compound. With benzalacetophenone there was isolated 2-phenyl-2-triphenylgermylethylphenyl ketone, m.p. 119-120°. This product was probably formed by a 1,4- addition of the triphenylgermyllithium to the conjugated unsaturated system. No addition product was isolated with trans-stilbene, octene-1 or cyclohexene.

Triphenylgermyllithium reacted with benzophenone anil to give an unknown addition product melting at 214-215°. The infrared spectrum of this addition product showed the characteristic phenyl-germanium absorption peak; however, there were no N-H or aliphatic C-H absorption peaks, thus ruling out 1,4- or 1,2- addition. With benzalaniline there was obtained triphenyl- $\alpha$ -anilinobenzylgermane, m.p. 123-124°. There was no reaction with benzonitrile, pyridine, or quinoline. With azobenzene there was isolated an unknown addition product melting at 143-143.5°. The infrared spectrum of this addition product showed a characteristic N-H absorption peak as well as the phenyl-germanium absorption band. With acetaldehyde the product found was triphenyl-1-hydroxyethylgermane, m.p. 105-106°; however, no product was isolated with benzaldehyde.

Triphenylgermyllithium reacted with ethylene oxide to give triphenyl-2-hydroxyethylgermane, m.p. 93.5-95°. With propylene oxide there was isolated triphenyl-2-hydroxypropylgermane, m.p. 93.5-95°, and with styrene oxide there was found triphenyl-2-hydroxy-2-phenylethylgermane, m.p. 139-140°.

Triphenylgermyllithium was found to metalate fluorene to give 9-fluorenyl-

<sup>1</sup>Doctoral thesis number 1772, submitted March 9, 1956.

Chairman of Committee, Henry Gilman, Department of Chemistry.

<sup>2</sup>B.S., University of Detroit, Detroit, Michigan.

Research Associate, Industrial Science Research Institute.

lithium. Reaction with bromine gave only hexaphenyldigermene, thus ruling out the possibility of a dissociation of triphenylgermyllithium into diphenylgermanium and phenyllithium.

Triphenylgermane, with peroxide initiation, added to octadecene-1 to give triphenyl-n-octadecylgermane and added to triphenylallylgermane to give 1,3-bis-(triphenylgermyl)-propane, m.p. 135-135.5°. With methylolithium, triphenylgermane gave a 77 per cent yield of triphenylgermanecarboxylic acid after carbonation, and with butyllithium a quantitative yield of the same acid was isolated. With triphenylgermyllithium, triphenylgermane gave a small amount of hexaphenyldigermene. This is in contrast with trisubstituted silanes which react with organolithium reagents to give the unsymmetrical tetra-substituted silane and lithium hydride.

In order to study the strengths of bonds between various Group IV-B elements triphenylgermyltriphenylsilane, m.p. 354-355°, was prepared and found to be inert to iodine and oxygen; it was cleaved by sodium-potassium alloy to give triphenylgermylpotassium and triphenylsilylpotassium. Triphenylgermyltriphenyltin, m.p. 286-289°, was prepared and was found to be inert to oxygen; however, it was cleaved by iodine at room temperature and by sodium-potassium alloy in the presence of tetrahydrofuran. Hexaphenyldigermene was found to be inert to oxygen and iodine; however, it was cleaved by sodium-potassium alloy in the presence of an initiator. These results are in contrast to hexaphenylethane which is readily cleaved by oxygen and by iodine, and which spontaneously dissociates into triphenylmethyl free radicals.

Other new organogermanium compounds prepared were: triphenyl-2-phenylethylgermane, m.p. 148-149.5°; triphenyl-3-phenylpropylgermane, m.p. 71-72°; triphenylallylgermane, m.p. 90-91.5°; triphenylchloromethylgermane, m.p. 117-118.5°; triphenyl-alpha-bromobenzylgermane, m.p. 140.5-141.5°; and diphenyl-bis-(beta-phenylethyl)-germane, m.p. 60.5-61°.

The triphenyl-alpha-bromobenzylgermane was prepared by the reaction of triphenylbenzylgermane with N-bromosuccinimide. The reaction of N-bromosuccinimide with triphenyl-2-phenylethylgermane gave only a mixture from which there was isolated triphenyl-beta-styrylgermane, m.p. 147-148.5°.

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## CHURCH LEADERSHIP IN POLK COUNTY, IOWA<sup>1</sup>

Hugh W. Ghormley, Sr.<sup>2</sup>

Department of Economics and Sociology

This report presents some of the findings of a study of church leadership as related to certain other factors, based on data gathered in the summer of 1948 in Polk County, which is now identified as the Standard Metropolitan Area of Des Moines, Iowa. Information was gathered by interviews in 1297 households, constituting a stratified random sample drawn on an area basis. The analyses included in this report were based on data concerning a residual sample of 2485 individuals on whom information was complete on the points studied.

In addition to church leadership, attention was given to two other forms of church participation, church membership and church attendance. Four addi-

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<sup>1</sup>Doctoral thesis number 1738, submitted December 2, 1955. Chairman of Committee, Ray E. Wakeley, Department of Economics and Sociology.

<sup>2</sup>A.B., Drake University, Des Moines, Iowa. M.A., *ibid.* B.D., *ibid.* M.S., Iowa State College, Ames. Associate, Agricultural Experiment Station.

tional factors were studied in relation to the three participation factors: sex, age, occupational status, which was used as an index of social stratification, and residential mobility.

Church leaders were identified for purposes of the study as professional or lay persons who had been elected or appointed to one or more positions of leadership of any rank down to and including the chairmanship of a committee of the church or a related religious group.

Because of differences in the definition of church membership, only individuals fifteen years old or older were considered. Above this age, however, the various churches' definitions of membership were accepted. Churches in which membership was held were identified as of the following types: 1) Non-council Protestant, i.e., bodies not members of the Iowa Council of Churches, 2) Council-affiliated Protestant, 3) Roman Catholic, 4) Jewish, and 5) Other.

Church attendance was studied in terms of the reported number of religious services connected with the church that were attended during June, 1948.

Residential mobility was represented by comparison of place of residence in 1948 with that in 1940. Four categories were distinguished: 1) no change of residence, 2) intrazone, i.e., movement within one of the ten types of area into which the county had been divided for the stratification of the sample, 3) interzone, i.e., movement from one type of area to another, 4) intercounty, i.e., movement into Polk County from any other location.

All church leaders were church members. Churches of all types except the Roman Catholic did not differ significantly in ratio of leaders to nonleader members; the ratio was relatively very low among Roman Catholics. Church leaders attended much more frequently than nonleaders. Church members attended more frequently than nonmembers. Church types ranked in frequency of attendance: 1) Roman Catholic, 2) Noncouncil Protestant, 3) Other, 4) Council-affiliated Protestant, 5) Jewish.

Females had a higher proportion of church members than males. Church types did not vary significantly in sex ratio. Females attended church more frequently than males. The ratio of leaders to nonleader church members did not vary significantly with sex. Church types did not vary significantly in sex ratio among leaders. Among nonattendants, more females than males were church members. Among attendants, the sexes did not significantly differ in proportion of members. Sex differences in the relationship between attendance and membership in specific types of churches were not significant. There was no significant sex difference in relationship of leadership to attendance.

Age categories ranked in ratio of members to nonmembers: 1) 45 to 54, 2) 55 to 64, 3) 15 to 24, 4) 35 to 44, 5) 65 or over, 6) 25 to 34 years. There were relatively few Council-affiliated Protestants aged 15 to 24 or 45 to 54, or Roman Catholics aged 55 years or over. Age categories ranked in attendance: 1) 15 to 24, 2) 45 to 54, 3) 55 to 64, 4) 35 to 44, 5) 65 or over, 6) 25 to 34 years. Age categories ranked in ratio of church leaders to nonleader church members: 1) 55 to 64, 2) 45 to 54, 3) 35 to 44, 4) 15 to 24, 5) 25 to 34, 6) 65 years or over.

Occupational categories ranked in ratio of church members to nonmembers: 1) persons doing their own housework, 2) students, 3) professional workers, etc., 4) skilled workers, 5) laborers and service workers, 6) unemployed, Jews ranked relatively high in occupational status, and noncouncil Protestants ranked relatively low. Occupational status groups ranked in church attendance: 1) students, 2) those doing their own housework, (3.5) professional workers, etc., (3.5) skilled workers, 5) laborers and service workers, 6) unemployed. Occupational categories ranked in ratio of church leaders to nonleader church members: 1) professional workers, etc., 2) persons doing their own housework, 3) students, 4) skilled workers, 5) unemployed, 6) laborers and service workers.

Mobility categories ranked in ratio of church members to nonmembers:



1) no change, 2) intercounty, 3) interzone, 4) intrazone. Noncouncil Protestants and Roman Catholics were relatively numerous in intrazone and interzone categories, and relatively few in "no change" and intercounty categories. Council-affiliated Protestants varied in exactly the opposite way. Jews had a very high proportion reporting no movement. The Other group was high in movement between zones. Mobility categories ranked in church attendance: 1) no change, 2) interzone, 3) intrazone, 4) intercounty. The ratio of church leaders to nonleader members was not found to be significantly related to residential mobility.

## MULTI-BAND ELECTRICAL CONDUCTION<sup>1</sup>

John Browning Gibson<sup>2</sup>

Department of Physics

Thermally induced electronic scattering is of importance in transport phenomena in metals. The probability of thermally induced scattering in nickel from a 4s state near the Fermi level to either a 4s or a 3d state near the Fermi level has been computed. The method of the deformable potential was used, but the potential was adjusted to account for the correct zero of potential in a homogeneously deformed crystal and to take care of charge redistribution in an inhomogeneously deformed crystal. 4s electrons are considered in the weak binding approximation, 3d electrons in the strong binding approximation.

When the difference of the initial and final electronic propagation vectors,  $\vec{k}_i - \vec{k}_f$ , is small, normal scattering takes place. As  $\vec{k}_i - \vec{k}_f$  increases, Umklapp scattering must be averaged with increasing weight with the normal scattering, so that when  $\vec{k}_i - \vec{k}_f$  is on the Brillouin zone boundary, the weight factors are equal. When  $\vec{k}_i - \vec{k}_f = \vec{K}$ ,  $2\pi$  times a reciprocal lattice vector, scattering is completely Umklapp.

The amplitude calculated for 4s - 4s Umklapp scattering is similar to that of normal scattering but larger by about a factor of 0.8  $(KE)_0/\zeta = 8$ , where  $(KE)_0$  is the kinetic energy of conduction electrons at the bottom of the band and  $\zeta$  is the Fermi energy relative to the bottom of the band. This large value seems unreasonable, and indicates that this method is probably not very accurate for large angle scattering.

The amplitude for 3d - 4s scattering is of comparable size with that for 4s - 4s scattering. For a given initial state, the calculations show that 3d - 4s scattering is angularly dependent both in polar and azimuthal angles of  $\vec{k}_i - \vec{k}_f$  relative to  $\vec{k}_i$ . 4s - 4s scattering is dependent only on the angle between  $\vec{k}_i$  and  $\vec{k}_f$ .

<sup>1</sup>Doctoral thesis number 1713, submitted August 16, 1955.

Chairman of Committee, Joseph M. Keller, Department of Physics.

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PILOT PLANT PRODUCTION OF  
HAFNIUM-FREE ZIRCONIUM BY ADSORPTION<sup>1</sup>Robert Henry Giffen<sup>2</sup>

Department of Chemical Engineering

The purpose of this investigation was to design and operate a pilot plant for continuous separation of zirconium from hafnium, based upon the preferential adsorption on activated silica gel of hafnium compounds from a methanol solution of hafnium and zirconium tetrachlorides. The continuous adsorption column used to obtain the experimental data reported was 6 inches in diameter, filled with adsorbent to a depth of 65 inches. The column had a nominal capacity of 0.2 pound of purified zirconium per hour, and reduced the hafnium content of the zirconium from 20,000 to 100 ppm.

Feed solution composition and silica gel quality were held to specifications based upon prior investigation. The factor by which the hafnium to zirconium ratio was reduced, defined as the purification ratio, was observed to vary directly with the silica gel feed rate, and inversely with the product solution flow rate. Experimental values of the purification ratio were correlated with the ratio of the adsorbent bed volume to the product solution flow rate, and with the ratio of the silica gel feed rate to the product solution flow rate. The yield of zirconium was observed to vary inversely with the ratio of the silica gel feed rate to the product solution flow rate.

The results of the research were applied to the design of a proposed semi-works plant for the purification of one thousand pounds of zirconium per month. The product would be recrystallized, high-purity zirconyl chloride octahydrate containing less than one hundred parts of hafnium per million parts of zirconium.

Itemized cost estimates were made which indicated that zirconium could be processed in this proposed semi-works plant at a production cost of \$6.65 per pound of zirconium. Based upon information received from the Oak Ridge National Laboratory, a thiocyanate, liquid-liquid extraction plant, having the same capacity would involve production costs of \$10.14 per pound of zirconium.

This research provides the basic engineering data from which a semi-works plant for adsorption separation of zirconium from hafnium may be designed with confidence.

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<sup>1</sup>Doctoral thesis number 1244, submitted December 14, 1951. Chairman of Committee, G.H. Beyer, Department of Chemical Engineering.

<sup>2</sup>B.S., Newark College of Engineering, Newark, New Jersey. M.S., Iowa State College, Ames. Graduate Assistant, Institute for Atomic Research.

SOME CORRELATIONS BETWEEN ORGANOTIN COMPOUNDS  
AND THEIR ORGANOGERMANIUM ANALOGS<sup>1</sup>Lewis Alexander Gist, Jr.<sup>2</sup>

Department of Chemistry

The physical and chemical properties of analogous organic derivatives of tin and germanium have been compared. A simple linear relationship exists between the boiling points of organotin compounds and their organogermanium analogs; however, no simple relationship could be established for the refractive indices and densities of these analogs. In a general way, analogous organic derivatives of tin and germanium react similarly. The differences observed in the chemical properties of these derivatives have been attributed to the differences in the degree of reactivity rather than differences in the type of reaction.

The reaction of triphenyltinlithium with diethyl carbonate and with ethyl chloroformate have been explored as a possible route for preparing ethyl triphenylstannylcarboxylate and bis(triphenyltin) ketone. The products obtained, however, were not the desired ester and ketone. Instead, carbon monoxide was vigorously evolved, and hexaphenylditin (ca. 50 per cent) was obtained as the principle product along with a lesser amount (ca. 20 per cent) of tetraphenyltin.

Incidental to the preparation of m-hydroxyphenyl derivatives of tin, the reaction of n-butyllithium with m-bromophenol as well as m-chlorophenol was investigated. While m-chlorophenol fails to undergo a halogen-metal interconversion reaction, m-bromophenol reacted readily giving the expected lithium m-lithiophenoxide, which was identified indirectly through carbonation. The order of mixing the reagents had a pronounced effect on the yield of the final product. Better yields were obtained when n-butyllithium was added to m-bromophenol than when the reagents were mixed in the reversed order.

Lithium m-lithiophenoxide reacted smoothly with tin(IV) chloride to give a satisfactory yield (49 per cent) of tetra-m-hydroxyphenyltin, melting at 178-179°. Since organolithium derivatives reportedly cause cleavage and redistribution reactions with organotin halides (1), lithium m-lithiophenoxide was first converted to the corresponding Grignard reagent, then treated with the appropriate organotin chloride to obtain the following organotin compounds: Triphenyl-m-hydroxyphenyltin (50 per cent, m.p. 207-208°), diphenyldi-m-hydroxyphenyltin (35 per cent, m.p. 189-190°), and phenyltri-m-hydroxyphenyltin (41 per cent, m.p. 203-205°).

A 41 per cent yield of ethyl m-triphenylstannylphenoxyacetate (m.p. 97-98°) was obtained from the reaction of triphenyl-m-hydroxyphenyltin with ethyl bromoacetate, while ethyl chloroacetate did not react under analogous conditions.

An attempt was made to prepare organotin dyes through the coupling of triphenyl-m-hydroxyphenyltin with p-substituted benzenediazonium fluoborates. In the absence of a buffer, p-nitro, p-bromo, and p-carboxybenzenediazonium fluoborate did not react, and the starting material (triphenyl-m-hydroxyphenyltin) was recovered in yields of 92, 86, and 89.5 per cent, respectively. In the presence of sodium carbonate as a buffer, the starting material was again recovered, but in poorer yields, along with a lesser amount of a red oil which was not resolved into any pure components.

<sup>1</sup>Doctoral thesis number 1759, submitted January 23, 1956.

Chairman of Committee, Henry Gilman, Department of Chemistry.

<sup>2</sup>B.S., Virginia Union University, Richmond. M.S., Howard University, Washington, D.C. Graduate Assistant, Industrial Science Research Institute.

Triphenyl-1-cyclopentadienyltin (71.5 per cent, m.p. 129-130°), diphenyl-di-1-cyclopentadienyltin (70 per cent, m.p. 105-106°), and phenyltri-1-cyclopentadienyltin (40 per cent, m.p. 64-65°) were prepared through the reaction of cyclopentadienylmagnesium bromide with the appropriate organotin chloride. The preparation of tetra-1-cyclopentadienyltin was also attempted, but the isolation of this derivative proved to be somewhat troublesome, and the product obtained decomposed before it was completely characterized.

The cyclopentadienyl derivatives of tin, prepared in this investigation were relatively unstable. The rate of decomposition was dependent upon the number of cyclopentadienyl groups in the molecule; and, it was accelerated by both light and air.

Triphenyl-1-cyclopentadienyltin was readily cleaved at room temperature by water to give triphenyltin hydroxide [86.5 per cent, identified as bis(triphenyltin) oxide], by *n*-butyllithium to give tetraphenyltin (47 per cent), and by bromine to give triphenyltin bromide (52 per cent). The relative ease with which this derivative was cleaved by water made it desirable to purify these organotin compounds of cyclopentadiene without first hydrolyzing the reaction mixture. This was accomplished by digesting the concentrated reaction mixture with benzene-petroleum ether (b.p. 57-70°), and filtering the resulting suspension. After concentrating the filtrate, the product was obtained.

Triphenyl-1-indenyltin (54 per cent, m.p. 129-130°), and diphenyldi-1-indenyltin (29.5 per cent, m.p. 107-110°) were obtained from the reaction of the appropriate organotin chloride with indenylmagnesium bromide. These indenyl derivatives of tin were not hydrolyzed under conditions similar to those used for the hydrolytic cleavage of triphenyl-1-cyclopentadienyltin.

The Diels-Alder reaction of triphenyl-1-cyclopentadienyltin was investigated. From the reaction of this organotin compound with maleic anhydride, a 59 per cent yield of 7-(triphenylstannyl)bicyclo[2.2.1]-hept-5-ene-2,3-phenyl-1-cyclopentadienyltin reacted with diethyl maleate to give 7-(triphenylstannyl)bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic acid diethyl ester (50 per cent, m.p. 107-109.5°), and with diethyl acetylenedicarboxylate to give 7-(triphenylstannyl)bicyclo[2.2.1]-hepta-2,5-diene-2,3-dicarboxylic acid diethyl ester (44.5 per cent, m.p. 107-108°).

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SOME CORRELATIONS BETWEEN STRUCTURE AND THERMAL STABILITY OF ORGANOSILICON COMPOUNDS<sup>1</sup>Jack J. Goodman<sup>2</sup>

Department of Chemistry

One of the useful properties of many organosilicon compounds is their resistance to high temperatures. It was the purpose of this thesis to synthesize molecules of this type for possible use as lubricants at very high temperatures.

The materials prepared were of the tetra-substituted silane type. As a basis for determining the thermal stability of various organic groups, the phenyl-substituted silanes were used. When one or more phenyl groups were replaced by a different organic moiety, the change in the high temperature resistivity was then ascribed to the new group. The compounds were placed in a capillary tube inserted into an electrically-heated copper block. A part of the tube extended above the block and a measure of the volatility could be made by noting condensation or refluxing in this portion. Discoloration of the sample during the heating process was noted as one evidence of decomposition.

Several series of compounds were prepared and tested for thermal stability. The general reaction was one between an organometallic reagent and a halo-silane such as diphenyldichlorosilane, trichlorosilane, etc. Diphenyl-bis-(*m*-trifluoromethylphenyl)-, phenyl-tris-(*m*-trifluoromethylphenyl)- and tetrakis-(*m*-trifluoromethylphenyl)-silane had melting points of 96-97°, 80-81°, and 102-103°, respectively. These compounds volatilized in the range 362-380° with very little discoloration. The entire series from triphenyl-*m*-tolyl-through tetrakis-*m*-tolylsilane was synthesized. The melting points in order of increasing number of *m*-tolyl groups were 150-151°, 119-120°, 128-129°, and 150-151°. Vaporization temperatures were in the range 420-425°. The color of the compounds at this temperature was generally pale to deep amber. It is to be noted that replacement of the hydrogen atoms in the methyl group on the benzene ring by fluorine atoms led to a decrease in the volatilization temperatures (about 50°) and a decrease in discoloration at these temperatures. The 9-fluorenyl containing compounds became deep red at or near their melting points. Diphenyl-bis-(9-fluorenyl)- and phenyl-tris-(9-fluorenyl)-silane had melting points of 270-271° and 333-334°, respectively. The preparation of the tetrakis-(9-fluorenyl)-silane was unsuccessful. This may be due primarily to steric factors. The *p*-phenoxy-phenyl series showed the most promise for high temperature stability. Diphenyl-bis-(*p*-phenoxyphenyl)-silane, m.p. 162-163°, phenyl-tris-(*p*-phenoxyphenyl)-silane, m.p. 149-150°, and tetrakis-(*p*-phenoxyphenyl)-silane, m.p. 206°, all volatilized in the range 505-560° with little discoloration.

Tris-(*m*-trifluoromethylphenyl)-silane, b. p. 147-150° at 0.05 mm,  $n_D^{20}$  1.4948,  $d_{20}^{20}$  1.3500 and tris-(*p*-trimethylsilylphenyl)-silane, m.p. 159-160° were prepared. It was intended to treat these compounds with organolithium reagents in order to obtain molecules of the type  $R_3SiR'$ . (1) None of the desired compounds were synthesized. Structures made by Fischer-Hirschfelder-Taylor models substantiated the thought that steric factors may be responsible for the lack of interaction.

It can be seen that most of these compounds are solids melting at or above 100°. Since it was desirable to have the possible lubricants as liquids at room

<sup>1</sup>Doctoral thesis number 1696, submitted July 11, 1955.

Chairman of Committee, Henry Gilman, Department of Chemistry.

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temperatures, *n*-alkyl groups of the length  $C_{11}-C_1$  were incorporated into these molecules. These alkyl groups drastically lowered the melting points, yet had reasonable thermal stability. Tris-(*p*-phenoxyphenyl)-*n*-dodecylsilane, b.p. 315-320° at 0.004 mm volatilized at 423-425° at atmospheric pressure with slight discoloration. Tris-(*p*-trimethylsilylphenyl)-*n*-dodecylsilane, b.p. 210-218° at 0.005 mm (crystallizes only after standing for several months to a pale-yellow solid, m.p. 68-74°) vaporized at 390-392° at atmospheric pressure with a pale-amber color. A table listing the compounds synthesized and results of their stability tests was prepared.

Some reactions of pentaphenylchlorodisilane (2) were studied to compare them with those of analogous monosilanes. In general no differences were found. However, treatment of pentaphenylchlorodisilane with dilute (1 per cent and 5 per cent) ethanolic potassium hydroxide led to cleavage of the silicon-silicon bond as evidenced by the isolation of triphenylsilanol. The following compounds from this unsymmetrical disilane series were prepared: pentaphenylethoxydisilane, m.p. 211-212°, pentaphenylhydroxydisilane, m.p. 134°, pentaphenyldisilane, m.p. 128-129° and hexaphenyldisilane, m.p. 361-363°.

Some organogermanium and organosilicon-germanium compounds were prepared. Triphenyl-4-pentenylgermane, m.p. 37-38°, volatilized at 382-384° with a pale-yellow color. 1-Triphenylgermyl-5-triphenylsilyl-pentane, m.p. 137-138°, was vaporized at 435-437° with considerable decomposition. Tris-(triphenylgermyl)-silane (3) was prepared and tested. It was amber at the volatilization temperature of 410-414°. Tris-(triphenylgermyl)-triphenylstannylsilane was synthesized. This compound decomposes at 340-342°. An attempt to prepare tris-(triphenylgermyl)-triphenylplumbylsilane was unsuccessful.

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INHERITANCE OF COMBINING ABILITY IN BROMEGRASS,  
*BROMUS INERMIS* LEYSS<sup>1</sup>Dale B. Grissom<sup>2</sup>

Department of Agronomy

Topcross progenies of 18  $S_0$  clones of bromegrass and 10  $S_1$  segregates from each along with 13 other  $S_0$  topcrosses and nine named varieties were grown in solid seedings in a split-plot design with five replications. Families made up the whole plots with  $S_0$  and  $S_1$  selections as subplots within each whole plot. All entries were evaluated for forage yield, spring vigor, leaf disease infection, and leafiness percentage in 1954 and for forage yield only in 1955. Dry weather prohibited a second cutting in 1954; however, two cuttings were made in 1955. Forage yields were recorded on a green weight basis from a 15 square-foot area. Spring vigor was evaluated on a 1 (poorest) to 5 (best) basis. Leaf disease was recorded on a numerical basis with 1 (0-10 per cent leaf area killed) to 10 (90-100 per cent leaf area killed). Leaf percentage was calculated as the percentage of the total culmage which was leaves. All data were subjected to standard split-plot analyses to obtain information on the inheritance of combining ability and extent of segregation for combining ability. Estimates of heritability of combining ability were calculated by progeny-parent regressions. Results of the topcross progeny test were correlated with previous evaluations of the parental material in an effort to obtain information on the relationships between space-planted and solid-seeded performance. Other aspects investigated were the effect of inbreeding for one generation on combining ability and correlations between inbreeding depression and combining ability. Intercharacter relationships, as measured in the topcross progeny test, also were studied to determine selection possibilities on the basis of solid stands.

Statistically significant differences were obtained among topcross entries included in the test indicating that combining ability for forage yield, spring vigor score, leaf disease infection, and leafiness percentage is inherited. On a family mean basis, significant differences could be demonstrated only for leaf disease and spring vigor scores. Analyses of  $S_1$  selections on an individual family basis indicated that three of the 18 families appeared to be segregating for combining ability for forage yield on a two-year basis. Significant differences among  $S_1$  segregates within families were observed for 10 families for spring vigor score, seven families for leafiness percentage, and one family for leaf disease score, indicating that segregation for combining ability also occurs for these characteristics.

Heritability estimates, as calculated by the regression method, gave values of 16, 19, 46, and 48 per cent, respectively, for leaf disease reactions, leafiness percentage, spring vigor, and forage yield. Correlations between  $S_0$  and  $S_1$  progeny means ranged from 0.31 for leafiness percentage to 0.65 for two-year mean forage yields.

Correlations between  $S_0$  topcrosses seeded in solid stands and previous evaluations of the same clonal families were low and variable with a range of -0.36 for leafiness between  $S_0$  topcrosses and O.P. progenies spaced three by three feet to 0.45 for forage yield between  $S_0$  topcrosses and O.P. progenies in three-foot drilled rows. In general, correlations between  $S_0$  topcross performance and previous evaluations for forage yield were positive

<sup>1</sup>Doctoral thesis number 1733, submitted November 29, 1955. Chairmen of Committee, R.R. Kalton and I.J. Johnson, Department of Agronomy.

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but of very low predictive value.  $S_0$  topcrosses and previous evaluations of the clonal families showed, in the main, negative associations for spring vigor and leafiness scores. Almost no correlation was obtained between performance of  $S_1$  topcrosses in solid seedings and  $S_1$  progenies grown in spaced plantings of three by three feet.

Analyses of variance of forage yields and leaf disease scores showed topcrosses of  $S_0$  clones to be significantly higher, on the average, for these characters than  $S_1$  topcross progenies. The mean values for  $S_0$  and  $S_1$  were 4.19 and 3.99 pounds per plot and 4.18 and 3.93, respectively, for forage yield and leaf disease score. No differences in combining ability could be shown between generations for spring vigor score and leafiness percentage.

Inbreeding depression and combining ability for forage yield were positively correlated. There was also a tendency for the lower yielding  $S_1$  lines to give the better topcrosses. The correlation was -0.18 between  $S_1$  selections and their topcrosses for forage yield on a two-year mean basis.

All possible intercharacter correlations were calculated among characters measured in the topcross progeny test. Values obtained were either of no consequence or in the desired direction for efficient selection except one. Positive associations between leaf disease infection and early spring growth were obtained. This appears to be detrimental to simultaneous selection for these two characteristics.

It was suggested that a reciprocal recurrent selection series be set up to further study the inheritance of combining ability and the possibilities of genetic advance through selection. It was further suggested that some of the additional  $S_0$  clones tested be included in the series since some of these clones showed high combining ability for the characteristics studied.

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#### RESPONSE OF ALFALFA VARIETIES TO CUTTING TREATMENTS AND FERTILIZERS<sup>1</sup>

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Department of Agronomy

Alfalfa is becoming an increasingly important forage crop with a considerable number of new varieties, adapted to more or less specific environmental and management conditions. This study was undertaken to investigate the occurrence and evaluate the magnitude of some differential responses of alfalfa varieties to selected factors of field management.

Eight alfalfa varieties, Atlantic, A-224, Buffalo, Grimm, Ladak, Narragansett, Ranger, and Vernal, were fertilized with phosphorus and potassium alone and in combination; the nutrients were applied at rates of 53 and 100 pounds per acre per year, respectively. Each variety-fertilizer combination was harvested by two systems: the first, a hay management system, cut on a stage-of-bloom basis, and the second, a simulated grazing regime, cut on a plant-height basis. Response to the treatments was measured in terms of forage yield, P and K content of selected cuttings and stand survival at the conclusion of the study. The test was planted in 1953 and harvested during 1954 and 1955; two-year data were considered satisfactory because much of the alfalfa acreage in the Corn Belt is usually maintained for only two years.

<sup>1</sup>Doctoral thesis number 1775, submitted March 9, 1956. Chairmen of Committee, C.P. Wilsie and John I. Pesek, Department of Agronomy.

<sup>2</sup>B.Sc., Rutgers University, New Brunswick, New Jersey. M.Sc., *ibid*.

Yield results indicated that:

1. Though not statistically significant, responses of fair magnitude were obtained under P fertilization, and smaller yield responses were noted when K or PK were applied.
  2. Considerable differences were noted in varietal yield, with Vernal and Narragansett the highest yielding and Ladak the lowest yielding of the varieties.
  3. The frequent-cutting system markedly reduced yields, particularly in the second season.
  4. The interaction between varieties and fertilizer treatments indicated that response to P fertilization varied to a considerable extent among varieties. A-224, Buffalo, Grimm, and Ladak responded to the greatest extent.
  5. The varieties responded differently to P application when cut for hay or clipped frequently. Grimm had a high positive response to phosphorus under both cutting systems, but Narragansett and Vernal, though high-yielding when cut for hay, yielded less under P fertilizer, when clipped frequently, than when not fertilized.
  6. The response noted in the two years, 1954 and 1955, differed markedly.
  7. Phosphorus or potassium fertilization increased the content of the respective nutrient in the forage, and the increase was greater in some varieties than in others.
  8. The per cent phosphorus in the forage of the eight varieties was depressed by potassium fertilization, with the exception of Buffalo, in which case the P content was increased.
  9. Vernal alfalfa differed from Buffalo and Grimm in that, although lowest in P content at the beginning of the season, by the end of the year, 1954, it ranked between Buffalo and Grimm. The varieties differed significantly in the total P content during the 1954 season.
  10. There were no significant differences in the total K content, during 1954, among the varieties Buffalo, Grimm, and Vernal.
  11. The K content of the varieties differed when cut for hay or clipped frequently as well as when fertilized with both phosphorus and potassium.
  12. The average number of surviving crowns, in the fall of 1955, was ten. Both crown number and the relative vigor of the crowns varied with fertilizer treatment, variety and combinations of these with cutting treatments.
  13. Alfalfa stand levels were not reflected in the field data and, though statistically significant, were of dubious predictive value.
  14. The results of this study are best considered preliminary in nature and the nutritional, physiological, or practical application of the results must be determined by future investigation.
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# STERIC EFFECTS ON THE FORMATION CONSTANTS OF METAL CHELATES OF BETA-DIKETONES<sup>1</sup>

Gerald A. Guter<sup>2</sup>

Department of Chemistry

Relative formation constants of metal chelates of the three beta-diketones, acetylacetone, diisobutyrylmethane, and dipivaloylmethane (DPM) were measured in 75 per cent water-dioxane in order to determine steric effects in chelation. These constants with the pKa of the reagent are given in Table I.

Table I. Formation constants of beta-diketones

Metal	Acetylacetone 11.27*			Diisobutyrylmethane 12.48*			Dipivaloylmethane 14.48*		
	logK <sub>1</sub>	logK <sub>2</sub>	logK <sub>1</sub> /K <sub>2</sub>	logK <sub>1</sub>	logK <sub>2</sub>	logK <sub>1</sub> /K <sub>2</sub>	logK <sub>1</sub>	logK <sub>2</sub>	logK <sub>1</sub> /K <sub>2</sub>
Cu (II)	11.57	9.64	1.90	12.29	9.99	2.30	13.91	11.55	2.36
Ni (II)	8.24	6.39	1.25	8.73	7.56	1.17	9.90	9.10	0.80
Co (II)	7.86	6.19	1.67	8.37	7.31	1.01	9.60	8.77	0.83
Mn(II)	6.81	5.18	1.63	7.23	6.07	1.16	8.34	7.44	0.90
Mg(II)	6.13	4.52	1.61	6.45	5.44	1.01	7.44	6.59	0.85

\*pKa value

The basicity of the enolate anion as well as the higher enol content of the more hindered reagents is explained on the basis of the steric requirements of the beta-diketones. A study of the ultraviolet spectra revealed a quantitative method for the measurement of the keto-enol equilibrium constant and the kinetics of enolization. A linear relationship between log enolization rates and pKa values of the diketones was observed. A similar linear free energy relationship was found to correlate enolization rates of beta-diketones and the rates of alkaline hydrolysis of corresponding aliphatic acid esters.

The steric effect in the formation of metal chelates is revealed in the following ways: For the square planar complexes, such as the copper (II) chelates, the separation factor becomes larger as the steric requirements of the ligand increase. The separation factors for the remaining metal chelates listed in Table I become smaller as the steric requirements increase. It would not be expected that these metals form square planar complexes. Models show that the maximum interference between ligands attached to the same metal ion will take place when a square complex is formed. The decrease in separation factors with increasing ligand bulk suggests that the larger ligand removes more water from the solvated metal atom during the first step in chelation and renders the monochelated metal more acidic toward the second ligand. The formation constants for the copper (II) chelates of the hindered reagents were smaller than would be expected from the basicity of the reagent.

The selectivity of DPM toward the lithium ion was explained on the basis of the steric requirements of the ligand and the small positive ion. A simple quantitative separation of lithium from sodium and potassium is made possible by the selectivity of DPM and the solubility of the lithium chelate of DPM in ether. A study of the infrared spectra of DPM and the lithium chelate shows the similarity of their structures.

<sup>1</sup>Doctoral thesis number 1703, submitted July 29, 1955.

Chairman of Committee, George S. Hammond, Department of Chemistry.

<sup>2</sup>B.A., Loras College, Dubuque, Iowa.

Fellow, Industrial Science Research Institute.



EVALUATION OF THE VETERANS ADMINISTRATION REHABILITATION PROGRAM FOR STUDENTS ENTERING IOWA STATE COLLEGE<sup>1</sup>Durwin Melford Hanson<sup>2</sup>

Department of Vocational Education

The purpose of this study was to investigate the academic achievement of male veteran and nonveteran students who entered Iowa State College without prior college experience. In order that the groups chosen might have had an opportunity to graduate, transfer to another college or university or drop out of school, the period from Winter Quarter 1944 through the Spring Quarter 1953 was selected for the study.

Classification of students for purposes of this study, was made into three groups, namely, those enrolling under the provisions of Public Law 16, Public Law 346, and those who entered without assistance from the Veterans Administration, assumed to be nonveterans.

There were 769 veterans who enrolled at Iowa State College under the Vocational Rehabilitation Act, Public Law 16. Of this number, 388 male veterans entered as freshmen without previous college experience. The median age at the time of entrance for this group was 22 years, 6 months. Thirty-four of the 388 were pursuing their education at the time of the study and were not included in this investigation. Also, the records were incomplete for four veterans, leaving a total of 350 veterans who had graduated, transferred, or dropped out of school by the Spring Quarter of 1953. Of this group, 181, or approximately 52 per cent, graduated from Iowa State College; 118, or 34 per cent, dropped out for personal or academic reasons; and 51, or 14 per cent, transferred to another college or university.

Of the approximately 12,500 veterans who entered Iowa State College, 1156 veterans under Public Law 346 were selected to be studied. Five hundred twenty-two male veterans entered as freshmen without previous college experience. The median age for this group was 21 years, 8 months. Of this total, 318 graduated, 120 dropped, and 84 transferred. The relationship in per cent of the number in each group to the total sample of 522 was used, and by random numbers the 350 actual cases to be studied were selected.

A total of 1237 male nonveteran undergraduate students' records were compiled. From this total of 1237, 809 students had enrolled at Iowa State College as freshmen without previous college experience. The median age for this group was 18 years, 6 months. Four hundred fifty-three, or approximately 56 per cent graduated; 218, or 27 per cent dropped; and 138, or 17 per cent transferred. Again the relationship in per cent of the number in each group to the total sample of 809 was used, and by random numbers the 350 cases selected.

Records for the 1050 students were complete with respect to the prematriculation information assembled from the American Council on Education Psychological Examination Quantitative Test, the American Council on Education Psychological Examination Linguistic Test, English Placement Test and the high school grade point average.

Evaluating the scholastic achievement of the three groups of students was the major purpose of this study. Two criteria were available from college records by which achievement could be evaluated. One criterion was the grade point average from the course marks which the student had received.

<sup>1</sup>Doctoral thesis number 1773, submitted March 9, 1956. Chairman of Committee, James E. Wert, Department of Vocational Education.

<sup>2</sup>B.S., Iowa State College, Ames. M.S., *ibid*.  
Assistant Professor, Engineering Extension.

A second criterion was the survival-attrition tendency as evidenced by a student's graduating from Iowa State College, transferring to another college or university, or dropping out of college for personal or academic reasons.

The similarity of these two criteria was shown by computing the triserial coefficients of correlation between grade point averages and the survival-attrition tendency as here defined. For each of the three groups, these triserial coefficients of correlation were

For Public Law 16 students, 0.8997  
For Public Law 346 students, 0.8512  
For nonveteran students, 0.8912.

These high correlations indicate the similarity of the two criteria employed in this study.

With grade point average, the first criterion, the means, without considering existing differences in student aptitude, were

For Public Law 16 students, 2.096  
For Public Law 346 students, 2.230  
For nonveteran students, 2.202.

The t-test for significance between the PL-16 and PL-346 students indicated the greater achievement for the PL-346 group, significant at the 5 per cent level whereas differences between the PL-16 and nonveteran students as well as differences between the PL-346 and nonveterans failed to meet the usual requirements for significance at the 5 per cent level.

An analysis of covariance was then made to evaluate differences among groups in grade point averages when student aptitude as indicated by high school average and English Placement score were controlled. The means adjusted for group differences in aptitude were:

For PL-16 and nonveteran students, 2.203 and 2.095, respectively  
For PL-346 and nonveteran students, 2.293 and 2.157, respectively  
For PL-16 and PL-346 students, 2.127 and 2.189, respectively.

The first two of these comparisons were significant, whereas, with the last comparison the difference was nonsignificant.

For the purpose of predicting grade point average, it was found that the high school grade point average and the English Placement percentile score yielded the most satisfactory prediction. For nonveteran students the most satisfactory equation was:

$$Y = 0.455X_1 + 0.007139X_4 + 0.62588$$

where  $Y$  = grade point average;  $X_1$  = high school grade point average, and  $X_4$  = English Placement percentile score.

A grade point average prediction table was developed whereby the grade point average could be predicted when given the high school grade point average and the score from the English Placement Test. The table indicated that with a high school grade point average of 3.4 and a score of 80 on the English Placement Test, the prediction grade point average was 2.66 for nonveteran students. Adjustment could be made by adding 0.16 to any prediction for a Public Law 346 student and 0.09 for a Public Law 16 student. The coefficient of multiple correlation of 0.5539 indicated limitations to a prediction for any given entering freshman, the standard error of estimate being 0.374.

Survival-attrition, as here defined, was the second criterion of achievement. In the three groups of 350 students the number graduating from Iowa

State College, number transferring, and the number dropping out of college were, respectively:

For PL-16 students, 181, 51, and 118

For PL-346 students, 214, 56, and 80

For nonveteran students, 197, 60, and 93.

When these discrepancies were evaluated, without control by the use of student aptitude variables, by Chi-square, only one of the three possible comparisons, PL-16 and PL-346 students, was significant at the 5 per cent level.

Student aptitude was, then, controlled by using high school averages and English Placement scores through discriminant analysis. With such control, the PL-16 students excelled the nonveteran students, contrary to the comparison without control of student aptitude. The difference was significant at the 1 per cent level. The PL-346 students were significantly superior to either the PL-16 students or the nonveteran student when evaluated in terms of survival-attrition tendency when student aptitude was controlled.

Based upon the English Placement scores and high school averages, the chances in 100 of a student graduating will vary from 26 to 80 for nonveteran students; from 34 to 87 for PL-346 students; and from 28 to 83 for PL-16 students. For convenience of counselors, a probability table was prepared for indicating the chances in 100 of a student graduating, transferring, or dropping out of college for various high school averages and English Placement percentiles.

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## SHELTER-ENVIRONMENTAL INFLUENCE ON SWINE GROWTH<sup>1</sup>

Thamon E. Hazen<sup>2</sup>

Departments of Agricultural Engineering  
and of Theoretical and Applied Mechanics

The objective of this work was to establish both theoretical and experimental relationships between various physical measurements of a naturally varying environment such as air temperature, thermal radiation, relative humidity, and animal responses measured by feed efficiency and average daily gain of swine when housed in similar buildings but having different environments resulting from a difference in the building covering material. Of secondary importance was to compare these findings with those under controlled conditions as reported by others. This study presents an analysis of heat transfer relationships and reports on the findings of the first summer and winter tests in buildings designed for the investigation.

Nine houses were constructed, identical in design with the exception of the covering material, each house having four pens measuring 8 feet by 8 feet with separate watering and feeding equipment in each pen. Two additional units were also constructed to serve as feed and bedding storage and to act as guard units, thus providing end animal units with the same exposure as those intermediate. Equipment and utilities were selected on the basis of special

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<sup>1</sup>Doctoral thesis number 1800, submitted May 31, 1956. Chairmen of Committee, Henry Giese, Department of Agricultural Engineering, and Glenn Murphy, Department of Theoretical and Applied Mechanics.

<sup>2</sup>B.S., Oklahoma Agricultural and Mechanical College, Stillwater. M.S., Purdue University, Lafayette, Indiana. Instructor.

design to assure uniformity of ventilation, drinking water temperature, and heat from other than animal sources inside the units. Covering materials selected were corrugated embossed aluminum, corrugated galvanized steel, and wood carsiding with an asphalt shingle roof over solid sheathing, three units of each covering material constructed.

The summer test used 72 pigs averaging 110 pounds each at the start and carried over an 8-week period to an average final weight of approximately 205 pounds each. The winter test used four animals per pen, 144 in all, starting at approximately 45 pounds each and continuing through an 8-week period to approximately 155 pounds each.

Thermocouple measurements of the inside air temperature at different levels, with the majority of these thermocouples at the animal level (6 inches above the floor), thermocouple measurements of the inside surface temperatures of the walls and roof, and hygrothermograph readings of relative humidity were recorded continuously in one unit of each of the three types. Periodic measurements at selected test points were taken in the remaining six houses to provide reliability of projection of the continuously recorded measurements to all houses. Radiometer readings of the various inside surfaces, to aid in the measurement of surface emissivities, and surveys of the interiors with the radiometer from a standard position, to give an index of thermal radiation intensity, were also taken periodically.

Animals were selected for nearly equal hereditary and growth characteristics, randomly placed in the houses, fed the same ration, provided the same temperature of drinking water, and managed as uniformly as possible. Animal weight and feed consumption were recorded at 2-week intervals. Free-choice of feed and water was practiced, special techniques and equipment designs described.

During the summer study animals in the aluminum covered units where temperatures were lowest had the most rapid growth and the highest feed efficiency, gaining 0.2 pounds per day more on 0.18 pounds less feed per pound of gain than those in the galvanized steel, and about 0.1 pounds per day more gain on 0.1 pounds less feed per pound of gain than those in the wood. These differences were found to be significant in the comparison of aluminum and galvanized steel, and not significant between aluminum and wood or wood and steel.

No significant differences were found in either average daily gain or feed efficiency during the winter study although there were measurable differences in environments between the house types.

Average inside air temperature at the animal level was found to be sufficiently dependent on other temperatures that it could be used as a criterion for judging environment. A correlation designed to eliminate natural growth effects on feed efficiency and average daily gain gave a highly significant comparison of this measurement between approximately sunrise and sunset and that of average daily gain, but a low correlation coefficient value when compared with feed efficiency. Coupled with a decline in feed consumption with temperature rise, this indicated the effect of a rise in temperature during the summer on heavy pigs to be a reduction in appetite.

Comparison of the animal responses in the summer study with those reported by others using controlled conditions shows good agreement for the same mean temperature range, but pigs in the winter study performed noticeably better in terms of feed efficiency and rate of weight gain if judged by values reported for similar mean temperatures under controlled conditions.

Difficulty was encountered in establishing the inside surface emissivity values due to the continual change of dirt and manure accumulation. Sensitivity of the relative humidity equipment was also affected by dust accumulation and an experimental wet-bulb unit to correct this trouble is discussed. The radiometer showed influence of effects other than thermal radiation which reduced the value of measurements thus obtained.

The presence of wet floors and substantial cooling of the building during the nights are believed to have been largely responsible for the better than anticipated summer gains and feed efficiencies.

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COLLEGE-LEVEL TELECOURSES FOR CREDIT: AN EXAMINATION  
OF A NEW ASPECT OF ADULT EDUCATION, WITH EMPHASIS  
ON THE ACTIVITIES OF WOI-TV<sup>1</sup>

Harry Eugene Heath, Jr.<sup>2</sup>

Department of Vocational Education

This study was designed to provide needed information concerning the college-level telecourse<sup>3</sup> for credit, i.e., its procedures, problems, and present state of development. Personal interviews and mail questionnaire returns were the primary sources of data. Specifically, the purposes of the study were:

1. To describe the development of college-level telecourses for credit by the Iowa State College Station, WOI-TV, and the techniques and problems of their presentation.
2. To describe the characteristics of the "credit audience" for certain telecourses presented by Iowa State College and Iowa State Teachers College through WOI-TV.
3. To present an audience evaluation of the nine telecourses offered by WOI-TV from Winter Quarter, 1953, through Winter Quarter, 1955.
4. To provide a basis for comparison of the modus operandi of 18 other four-year colleges and universities with that of WOI-TV.

The telecourse objective of WOI-TV has been to extend the educational benefits of Iowa State College beyond the limits of the campus. Certain criteria have been used in selecting telecourses to be broadcast. Among these criteria are the following:

1. The course should have few, if any, prerequisites.
2. Whenever possible, it should be general in its audience appeal.
3. An acceptable instructor should be available.
4. The course should be a rewarding educational experience for noncredit as well as credit viewers.

Iowa State Teachers College, with a teacher-training objective, has based its selection of telecourses upon the "stated needs of students," but also has made an effort to conform, insofar as possible, to the four criteria listed above.

Of the 209 students accounting for 292 registrations in the study, 93.3 per cent were female, with a mean age of 39.8 years. Most (79.4 per cent) were married; 11.0 per cent were single, and 9.6 per cent widowed. When

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<sup>1</sup>Doctoral thesis number 1808, submitted June 4, 1956. Chairman of Committee, Barton Morgan, Department of Vocational Education.

<sup>2</sup>B.A., University of Tulsa, Tulsa, Oklahoma. M.S.J., Northwestern University, Evanston, Illinois. Assistant Professor, Technical Journalism.

<sup>3</sup>The term telecourse as used herein refers to direct teaching of a systematic nature by television for which official college credits are awarded.



compared with other Iowa females, those in the telecourse population were older by an average of 8.4 years. In terms of marital status, fewer women enrolled were unmarried than were those in the general population.

Enrollees had averaged 1.8 years of college work, although 21.1 per cent had not gone beyond high school. The educational level of the average telecourse student was approximately three years above that of Iowa's general population. As a corollary, most were from the middle and upper-middle socio-economic levels.

Television set ownership among telecourse students (89.3 per cent) was greater (by 15.1 per cent) than that for the state as a whole, and 9.4 per cent greater than for the WOI-TV service area. Despite this greater set ownership, telecourse students tended to view television an average of only 2.0 hours daily, considerably less than the average for the general population.

All but six of the 209 students favored the continuation of official credits for telecourse work, and 70.9 per cent said the use of credits for teacher certification was an important advantage. The composite grade-point average for all telecourses (2.4) was the same as for campus students at Iowa State College during the period covered by the research.

Nearly seven out of ten respondents reported putting the material learned in telecourses to practical use. Age and education did not appear to be a function of this attribute.

When compared with the mean scores calculated by Starrack<sup>1</sup> from student ratings of classroom teachers at Iowa State College, the telecourse instructors fared well on seven of nine attributes rated. However, telecourse students rated their instructors low for the lack of "original thinking demanded" in the courses and for their lack of an adequate "sense of humor" in their teaching approach.

Only 14.8 per cent of the respondents indicated they had difficulty in concentrating upon telecourse lectures. Ease of concentration tended to increase with age. With regard to note taking, 85.8 per cent said they took notes "most of the time." About one out of three found this to be "difficult." Only 6.6 per cent reported feeling isolated.

Teachers made their assignments effectively, despite the lack of two-way communication. When asked if assignments had been clearly stated, 94.2 per cent answered "yes." The grade received was "about right" in the opinion of 83.4 per cent of the respondents. Some (14.7 per cent) felt the grading too severe, and a few (2.9 per cent) too lenient. There were eight failures in 292 registrations.

In the survey of selected colleges and universities, only seven of the 16 responding institutions indicated they had formulated a long-range policy with regard to telecourses. The most comprehensive plan seemed to be that of Michigan State University. All institutions appeared to be highly concerned about protecting the academic integrity of the work.

Primary responsibility for telecourses among the responding schools was vested most frequently in the unit charged with extension education; however, an all-campus faculty committee usually was given an important voice in the selection of teachers and courses.

The teacher usually was selected on the basis of "classroom observation" of his work, and "informal faculty opinions." The teacher's interest in TV, his scholarly achievements, and his potential public relations value were factors generally taken into consideration. A reduced teaching load and/or additional pay were the most frequent rewards for telecourse teachers.

At the time of the survey, 12 institutions were using facilities donated by

<sup>1</sup>Starrack, James A. 1932. The construction of a scale for the measurement of college teaching and the determination of its reliability and validity. Unpublished Ed.D. thesis. Boston, Mass., Boston University Library. pp. 41, 51.

commercial stations, and four were broadcasting through their own facilities. In general, excellent cooperation was received from commercial stations.

Responding institutions had little qualitative evidence to offer in support of the success of their programs. Quantitatively, audiences ranged from an estimated 500 viewers to an estimated 70,000.

Respondents emphasized the need for telecourses to deal with the problems applicable to day-to-day living, and recognized that much remains to be done in encouraging formation of viewing groups and developing better promotional techniques to build larger viewing audiences.

Little reliable information was furnished on budgetary matters. Likewise, the data on cost per program was meager. The figures provided by six institutions ranged from \$10 to \$500, with the average \$141.

With few exceptions, the data from other schools were similar to those collected from WOI-TV officials. Production details were simple. One camera was used on the performer, and a second camera on visual aids. A minimum of camera movement was involved. The instructor followed his usual classroom pace in presenting the subject, but eliminated some of the supporting ideas and examples normally used. However, some institutions appeared to be further advanced than Iowa State College in basic planning for telecourse activities.

More research on the subject is needed, especially with regard to the behavior of noncredit viewers who follow such courses regularly.

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## THE ABSOLUTE INFRARED ABSORPTION BAND INTENSITIES OF THE METHYLENE GROUP VIBRATIONS OF SOME METHYLENE HALIDES<sup>1</sup>

Richard M. Hedges<sup>2</sup>

Department of Chemistry

The absolute intensities of the  $\nu_1$ ,  $\nu_6$ , and  $\nu_3$  bands of  $\text{CH}_2\text{F}_2$ ,  $\text{CH}_2\text{Cl}_2$ ,  $\text{CH}_2\text{Br}_2$ ,  $\text{CH}_2\text{ClF}$ , and  $\text{CH}_2\text{BrCl}$  were measured in the vapor phase using the pressure broadening method.

The absolute intensities of the  $\nu_1$  and  $\nu_6$  bands of  $\text{CH}_2\text{Cl}_2$ ,  $\text{CH}_2\text{Br}_2$ ,  $\text{CH}_2\text{I}_2$ , and  $\text{CH}_2\text{BrCl}$  were measured in  $\text{CCl}_4$  solution.

Normal Coordinate analyses were made for the interpretation of the vapor phase data. The vapor phase intensities were interpreted in terms of bond moments and bond moment derivatives assuming the additivity of bond moments. The results indicate that  $\mu_{\text{CH}}$  in these compounds is around  $0.1 \times 10^{-18}$  e.s.u.

The observations of the  $\nu_3$  band of  $\text{CH}_2\text{F}_2$  at  $1508 \text{ cm}^{-1}$  in the infrared supports the assignment of the  $1508 \text{ cm}^{-1}$  vibration as the  $\nu_3$  ( $A_1$ ) fundamental made previously on the basis of Raman effect data.

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<sup>1</sup>Doctoral thesis number 1715, submitted August 17, 1955.

Chairman of Committee, George S. Hammond, Department of Chemistry.

<sup>2</sup>B.S., Southern Methodist University, Dallas, Texas.

Research Assistant, Institute for Atomic Research.

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FERROMAGNETIC-ANTIFERROMAGNETIC PHASE TRANSITIONS<sup>1</sup>Thomas James Hendrickson<sup>2</sup>

Department of Physics

The problem of ferromagnetic-antiferromagnetic phase transitions for a system in which the angular momentum per atom has the magnitude  $J$  is studied in the molecular field approximation. Both ferromagnetic and antiferromagnetic interatomic interactions, which are slightly temperature dependent, are assumed to exist between certain nearby neighbor atoms. An anisotropy energy is introduced of the form which arises from the effect of crystal fields. The structure is subdivided into sublattices, and the partition function  $Z$  is derived. From  $Z$  are obtained the free energy  $F$  and the equations which determine the average angular momentum per atom of each of the sublattices.

Under the assumption that only first, second, and third nearest neighbor interactions are significant, various ordered arrangements are found for the hexagonal close-packed structure, when it is subdivided into six and into eight hexagonal sublattices and the applied magnetic field is zero.

The molecular field equations are solved for arbitrary magnitudes and directions of the applied magnetic field and for arbitrary temperatures, under the assumption that there are only two inequivalent angular momentum orientations in the crystal, so that the structure may be subdivided into just two sublattices. The relative stability of the various ordered states is investigated.

Calculations are made for  $J = 15/2$ , which corresponds to the case of dysprosium metal. The parameters giving the magnitude and temperature dependence of the molecular field coefficients are chosen so that the ferromagnetic-antiferromagnetic transition temperature, the Néel temperature, and the paramagnetic Curie temperature coincide with the values for dysprosium. The coefficient giving the magnitude of the anisotropy is selected so that the phenomenon of "spin flop" occurs for magnetic fields of the correct order of magnitude.

The theory predicts the following effects for single crystals. For temperatures in the antiferromagnetic range, a large anisotropy in the single crystal susceptibility is expected. The parallel susceptibility, for weak fields parallel to the preferred axis of alignment of the angular momenta, behaves like that of a normal antiferromagnetic, decreasing steadily with decreasing temperature. The perpendicular susceptibility for weak fields perpendicular to the preferred axis, increases strongly and monotonically as the temperature decreases. For temperatures in the antiferromagnetic range and for magnetic fields making small angles with the preferred axis, the phenomenon of "spin flop" occurs. The angular momenta undergo a sudden change in their directions of alignment as the applied magnetic field increases through a critical value and the corresponding magnetization curves are discontinuous. The temperature of the ferromagnetic-antiferromagnetic transition in magnetic fields parallel to the preferred axis is a strong function of the applied field, increasing with increasing field. For magnetic fields which exceed a certain critical value, the ferromagnetic-antiferromagnetic transition does not occur at all, and the system remains in the ferromagnetic arrangement for all temperatures.

The following results are obtained for polycrystalline dysprosium. The

<sup>1</sup>Doctoral thesis number 1760, submitted January 24, 1956.

Chairman of Committee, J.M. Keller, Department of Physics.

<sup>2</sup>B.S., University of Michigan, Ann Arbor. M.S., *ibid*.

Graduate Assistant, Institute for Atomic Research.

experimentally measured susceptibility, which for a polycrystalline sample is a weighted average of the susceptibilities parallel and perpendicular to the preferred axis in a single crystal, goes through a minimum at a temperature slightly below the Néel temperature, and then increases to very large values as the temperature decreases toward the temperature of the ferromagnetic-antiferromagnetic transition. The theoretical polycrystalline susceptibility shows qualitatively the same behavior. The sharp peak in the heat capacity at the temperature of the ferromagnetic-antiferromagnetic transition should become smeared out in the presence of large external magnetic fields. This should happen because the transition temperature for a single crystal depends strongly upon the orientation of the magnetic field relative to the crystal. A similar effect should appear at the Néel temperature, except that there the effect is less pronounced.

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SOME PHYSICAL-METALLURGICAL PROPERTIES OF  
SCANDIUM, YTTRIUM, AND THE RARE EARTH METALS<sup>1</sup>

Kenneth W. Herrmann<sup>2</sup>

Department of Chemistry

In the continuing effort to learn more about the nature of metals, the rare earth elements in particular, the crystal structures and precision lattice parameters of these metals were investigated. High purity metals were examined by powder, single crystal, and back reflection x-ray diffraction techniques. All but four of the back reflection samples were prepared by distillation in high vacuum (approximately  $2 \times 10^{-7}$  mm mercury). The back reflection examinations, by which very accurate lattice parameters can be determined, were considered necessary if quantitative comparisons of the properties of the rare earths are to be made. Although scandium and yttrium are not classified as rare earths, they were considered similar enough in their behavior to include them in this study. The crystal structures and lattice parameters of the metals investigated are given in Table 1.

From the crystallographic data of scandium, yttrium, and the rare earth metals the mole-atomic volume, density, axial ratio, and metallic radii were calculated for each element and then graphically compared. In addition to the expected variations in these properties throughout the series due to structure differences and the "lanthanide contraction," other irregularities were also observed. These cannot be satisfactorily explained at present.

Microscopic examinations of the distilled metals revealed strong evidence for the existence of twinning. Several photographs are presented.

Considerable confusion exists in the literature concerning the phase transformations exhibited by the lighter rare earth metals. To obtain further information concerning these phenomena the transformation temperatures of pure lanthanum, cerium, praseodymium, and neodymium were determined by investigating the electrical resistivities of these metals as a function of temperature. They were studied over the temperature range 20°C to approximately 20° to 100°C below their melting points. The data are presented in graphical form. Table 2 gives the resistivity values of the metals at 25°C and the transformation temperatures observed.

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<sup>1</sup>Doctoral thesis number 1723, submitted September 27, 1955.

Chairman of Committee, Frank H. Spedding, Department of Chemistry.

<sup>2</sup>B.S., Valparaiso University, Valparaiso, Indiana.

Research Assistant, Institute for Atomic Research.

Table 1. Lattice constants of scandium, yttrium and the rare earth metals

Element	Purity %	Crystal structure	Lattice constants (Å)		Standard error (Å)	
			a <sub>0</sub>	c <sub>0</sub>	a <sub>0</sub>	c <sub>0</sub>
Sc	99.6	h.c.p.	3.3090	5.2733	.0001	.0016
Y	99.4	h.c.p.	3.6474	5.7306	.0007	.0008
La	99.8	h.c.p.	3.770	12.159	.002	.008
Ce	99.9	f.c.c.	5.1612	---	.0005	---
Pr	99.9	h.c.p.	3.6725	11.8354	.0007	.0012
Nd	99.8	h.c.p.	3.6579	11.7992	.0003	.0005
Sm <sup>a</sup>	99	rhomb-h.c.p.	3.621	25.25	---	---
Eu	98-99	b.c.c.	4.606	---	.001	---
Gd	99.7	h.c.p.	3.6360	5.7826	.0009	.0006
Tb	99.9	h.c.p.	3.6010	5.6936	.0003	.0002
Dy	99.8	h.c.p.	3.5903	5.6475	.0001	.0002
Ho	99.4	h.c.p.	3.5773	5.6158	.0001	.0002
Er	99.8	h.c.p.	3.5588	5.5874	.0003	.0003
Tm	99.9	h.c.p.	3.5375	5.5546	.0001	.0004
Yb	99.9	f.c.c.	5.4862	---	.0004	---
Lu	99.9	h.c.p.	3.5031	5.5509	.0004	.0004

<sup>a</sup>Daane, A.H., R.E. Rundle, H.G. Smith, and F.H. Spedding. Acta Cryst. 7:532, 1954.

Table 2. Electrical resistivity and transformation temperatures of lanthanum, cerium, praseodymium and neodymium

Element	Trial no.	Transition cooling	Temperature (°C)		Resistivity at 25°C x 10 <sup>-6</sup> ohm-cm
			Heating		
La	1	340	320		56.8
La	2	340	320		
La	1	860.1	867.0		75.3
La	2	860.5	867.8		
Ce	1	726.3	733.5		68.0
Ce	2	726.2	733.7		
Pr	1	789.0	794.7		64.3
Pr	2	789.0	794.7		
Nd	1	861.1	863.7		64.3
Nd	2	861.2	861.7		

High temperature crystallographic studies still in progress have shown the intermediate phase of lanthanum to be f.c.c. with a lattice parameter of a<sub>0</sub> = 5.31 Å at about 260°C. At present no definite information concerning the high temperature structures has been obtained.



THE SUCCINOXIDASE SYSTEM IN MYROTHECIUM VERRUCARIA<sup>1</sup>James Lee Hilton<sup>2</sup>

Department of Botany

This investigation was undertaken to determine which essential respiratory enzymes could easily be extracted from a filamentous fungus for studies on the mechanism of fungicide action. Attempts to obtain intact mitochondria from *Myrothecium verrucaria* capable of oxidizing Krebs cycle intermediates were unsuccessful. However, particles prepared from mycelium and fortified with cofactors took up oxygen when incubated with pyruvate, citrate, ketoglutarate, succinate, fumarate, or malate. This would indicate that a Krebs cycle exists in the organism.

A detailed study was made of the succinoxidase system. Oxidation of succinate appeared to be catalyzed by a typical succinoxidase system associated entirely with the insoluble components of the cell-free extract. The Michaelis constant varied with the reaction conditions but was ca. 0.007 M under optimum reaction conditions with cytochrome c and glutamate added. A single sharp pH optimum was obtained at ca. 7.2 when the particles were saturated with cytochrome c. Without cytochrome c optimum pH varied from 6.8 to 7.2. Succinoxidase activity of the particles averaged 580  $\mu$ l O<sub>2</sub> taken up per hour per mg of particle nitrogen.

Inhibition of this enzyme system was obtained with malonate, fumarate, malate, oxalacetate, Cu, Co, cyanide, and 2-hydroxy-3-(2-methyloctyl)-1,4-naphthoquinone (SN5949). Succinoxidase activity was stimulated in the presence of cytochrome c, serum albumin, glutamate, and AMP, ADP, ATP, and UTP. A cation, probably Mg, was also required for stimulation by the nucleotides. It was concluded that this stimulation was due to removal of an endogenous competitive inhibitor of the dehydrogenase. This inhibitor appeared to be oxalacetate since glutamate, which was not oxidized, was generally more effective than ATP in stimulation of succinoxidase and in protection of succinoxidase against oxalacetate. The ATP protected succinoxidase against the inhibition of fumarate and malate as well as oxalacetate. The mechanism of the ATP protection is unknown. Succinoxidase inhibition by Co was also reduced in the presence of ATP but the adenylate had no effect on inhibition by Cu or malonate.

The quantity of succinoxidase extracted from the mycelium was sufficient for the enzyme system to have a major role in the respiration of the organism and it seemed likely that enough was present in the mycelium to support complete oxidation of glucose by an Emden-Meyerhoff-Krebs pathway. Inhibition of mycelial respiration by malonate, Co, cyanide, and SN5949 indicated that succinoxidase was essential for the respiration of the organism. However, mycelial respiration could, in time, recover from inhibition by SN5949. Non-reversible inhibition of the enzyme system was observed with this compound.

As a result of this study, an essential respiratory enzyme system, succinoxidase, has been extracted from the mycelium and monometric assay conditions for this system have been established which will allow quantitative comparison between different enzyme preparations. A known succinoxidase inhibitor, SN5949, tested under standard assay conditions gave comparable results among different enzyme preparations. It may be assumed then that this assay method can be used to compare toxicant effects on succinoxidase and mycelial respiration in studies to determine if succinoxidase is a site of respiratory inhibition by fungicides.

<sup>1</sup>Doctoral thesis number 1754, submitted December 9, 1955.

Chairman of Committee, F.G. Smith, Department of Botany.

<sup>2</sup>A.B., Duke University, Durham, North Carolina. M.S., Iowa State College, Ames. Graduate Assistant, Agricultural Experiment Station.

$C^{14}$ -TRACER STUDY OF THE WOHL-ZIEGLER  
BROMINATION OF CYCLOHEXENE<sup>1</sup>Marsha Hollander<sup>2</sup>

Department of Chemistry

The reaction of 1-cyclohexene-1- $C^{14}$  with N-bromosuccinimide was carried out both in refluxing carbon tetrachloride and in benzene at 45°. The preparation of 1-cyclohexene-1- $C^{14}$  involved the reaction of pentamethylene dibromide with sodium cyanide- $C^{14}$  to form pimelic nitrile-1- $C_2^{14}$  which was hydrolyzed, without isolation, by potassium hydroxide to pimelic acid-1- $C_2^{14}$ . This pimelic acid was converted into 1-cyclohexanone-1- $C^{14}$  by pyrolysis of its calcium salt. 1-Cyclohexanol-1- $C^{14}$  was then prepared by reduction of the cyclohexanone with lithium aluminum hydride. Reaction of the cyclohexanol with ethyl chlorocarbonate gave ethyl cyclohexyl-1- $C^{14}$ -1-carbonate which was pyrolyzed to 1-cyclohexene-1- $C^{14}$ .

In the case of the reaction in carbon tetrachloride, equivalent amounts of 1-cyclohexene-1- $C^{14}$  and N-bromosuccinimide were refluxed together for 45 minutes. The insoluble succinimide was filtered off under nitrogen pressure in an inert-atmosphere filtration apparatus. Most of the carbon tetrachloride was removed at atmospheric pressure through a Vigreux column. At 12 mm 6.34 g (46.3 per cent) of 3-bromocyclohexene-1- $C^{14}$ -x distilled at 59-60°.

The reaction in benzene at 45° was initiated by 2 mole per cent of 2,2'-azo-bis-2-cyclopropylpropionitrile. Forty minutes were required for completion of the reaction. After the succinimide was filtered off, the benzene was removed at -20° under a pressure of 2 mm through a column packed with 1/16 inch glass helices. Alcohol maintained at about -18° was circulated through the jacket surrounding the column. For the distillation of the 3-bromocyclohexene-1- $C^{14}$ -x the helices-packed column was replaced by a short Vigreux column to which was attached as a total-condensation head a dry ice condenser. The receiver was kept at -78°. The distilling flask was at -18° and alcohol at about the same temperature was circulated through the jacket surrounding the column. At a pressure of 0.007 mm 5.6 g (33 per cent) of 3-bromocyclohexene-1- $C^{14}$ -x was evaporatively distilled. The 3-bromocyclohexene-1 was kept at -78° under nitrogen until its reduction, which was carried out about 40 hours after the beginning of the bromination.

The 3-bromocyclohexene-1- $C^{14}$ -x resulting from each reaction was reduced to 1-cyclohexene-x- $C^{14}$  with lithium aluminum hydride. The cyclohexene was then converted to adipic acid-x- $C^{14}$  by ozonization followed by oxidation with hydrogen peroxide. Treatment of the adipic acid with a benzene solution of hydrazoic acid degraded it to carbon dioxide- $C^{14}$  and 1,4-diaminobutane-(?)1- $C^{14}$ . In each case radioanalysis of the adipic acid, carbon dioxide, and 1,4-diaminobutane showed three-fourths of the activity to be in the double bond.

No final conclusions concerning the mechanism of the Wohl-Ziegler reaction can be drawn from this work, for the same results would have been obtained not only if a mesomeric free radical were involved but also if formation of the 3-bromocyclohexene-1 by a mechanism not involving such an intermediate were followed by allylic rearrangement. Such rearrangement is possible even under the low-temperature conditions employed when the bromination was carried out in benzene.

<sup>1</sup>Doctoral thesis number 1777, submitted March 12, 1956.

Chairman of Committee, George S. Hammond, Department of Chemistry.

<sup>2</sup>B.S., University of Rochester, Rochester, New York. M.A., University of Toronto, Canada. Graduate Assistant, Industrial Science Research Institute.

PHYTOTOXICITY AND REACTIONS OF 2,2-DICHLOROPROPIONIC ACID<sup>1</sup>John Tucker Holstun, Jr.<sup>2</sup>

Department of Botany

The chemical, 2,2-dichloropropionic acid (DCPrA) is a relatively new herbicide. Since it appears to be readily translocated in plants it may be of considerable value in control of certain weeds, particularly perennial grasses and perhaps for selective weed control in crops. Its practical value will depend in part upon its reactions when used under a range of conditions that may affect either the herbicide or the plants to which it is applied. These investigations were conducted for the purpose of evaluating some of these reactions. Some of the factors influencing the leaching and decomposition of DCPrA in soils, the effects of two wetting agents on its phytotoxicity, and some factors influencing its translocation in plants were studied in a series of laboratory and greenhouse experiments.

Bioassays were used to indicate quantities of DCPrA in studies involving its leaching and decomposition in the soil. The growth of treated plants was used in other experiments as an indicator of its phytotoxicity as influenced by certain factors.

The response of soybeans grown in sections of soil columns previously treated with the equivalent of 24 lb per acre of DCPrA and then leached with 1.5 inches of water, indicated a high degree of mobility for the DCPrA in several soil types. Additions of manure or sand altered the leaching characteristics of the soils to a small degree. Added manure increased the retention, and added sand increased the mobility of the DCPrA.

Various factors were studied to determine their effect on the rate of decomposition of DCPrA in soil. A bioassay technique, based on the response of germinating millet seedlings, was used to estimate the quantity of DCPrA remaining in the soil after various intervals of time under varying conditions. Data were obtained which indicated that the decomposition of DCPrA in soils is primarily a direct function of an undetermined fraction of the microbiological population. Other factors influencing the decomposition rate were considered to act indirectly by affecting the activity of microorganisms in the soil. Decomposition of the herbicide appeared to be essentially halted for at least 16 weeks where the soil moisture or temperature was low. Adverse levels of pH or large additions of organic matter inhibited decomposition, but the inhibition appeared to be temporary. Where pH or organic matter additions were the only limiting factors, decomposition appeared to be practically complete in 8 to 16 weeks or less.

The soil type in which the highest rate of decomposition was found was a medium silt loam soil with low organic matter, that had been field limed to a pH of 6.5. The same soil type obtained from a nearby unlimed area, still in forest, had the slowest decomposition characteristics of all the soils studied.

The addition of two wetting agents did not appreciably increase the phytotoxic action of DCPrA applied as a foliage spray to young soybean plants, and one of the agents at high concentrations inhibited the effect of the high concentration of the herbicide. On corn the general effect of the wetting agents was to increase the activity. The lowest concentrations were fully as effective as the highest, and with one of the agents used, the lower four concentrations were more effective than the higher two. It was indicated that the effects of the additions of wetting agents were produced through a mechanism

<sup>1</sup>Doctoral thesis number 1699, submitted July 13, 1955.

Chairman of Committee, W. E. Loomis, Department of Botany.

<sup>2</sup>B.S., Alabama Polytechnic Institute, Auburn. M.S., *ibid*.

Graduate Assistant, Agricultural Experiment Station.

other than simple lowering of surface tension of the herbicide solution. A balance between absorption, injury at the point of application, and subsequent translocation to untreated plant parts appeared to be involved in the effects obtained by adding wetting agents to the herbicide.

Translocation of DCPra from treated to untreated shoots of quackgrass was increased by clipping the untreated shoots just prior to spraying, which indicated that translocation of DCPra occurred through the phloem, was not inhibited by a lack of high transpiration, and was perhaps increased by meristematic activity in the receiving tissues. In this experiment, chemically pure DCPra neutralized with NaOH was as toxic to quackgrass at a concentration of 50,000 ppm as 100,000 ppm of a commercially prepared research formulation of Na-DCPra which appeared to have a large excess of wetting agent.

The necessity for photosynthate in the translocation of DCPra under some conditions was indicated in an experiment where localized applications of DCPra failed to cause formative effects on new growth of starved plants unless sugar was added with the herbicide. In this experiment Na-DCPra and sucrose were applied separately or in combination to one leaf of starved or normal soybean seedlings. Starvation was obtained by holding the plants in darkness for 24 hours prior to and following treatment. The plants were treated by dipping one primary leaf into the appropriate solution. After 24 hours, the treated leaves were removed from the plant, and those plants that had been held in darkness were returned to normal light conditions. After 13 days injury symptoms were observed on the new growth of all plants grown in normal light and treated with the herbicide, either alone or with sucrose. Of the plants held in darkness, only those treated with both Na-DCPra and sucrose showed injury symptoms.

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## THE FORMATION OF THALLIUM CHLORIDE COMPLEXES AND THEIR EXTRACTION INTO ETHER<sup>1</sup>

Donald L. Horrocks<sup>2</sup>

Department of Chemistry

Thallium is one of a large group of elements which can be extracted into ethers from halogen acid solutions. The general lack of knowledge of the extraction process for these salts has given strong impetus to the study of all aspects of it.

Since there have been no previous investigations on the fundamental nature of the extraction of thallium-chloride complexes from HCl solutions, it was the purpose of this work to study the extraction under various conditions, using radio tracer techniques as the tool. This investigation, employing isopropyl ether, had as its immediate objective the determination of the empirical formula of the thallium compound in the ether phase and the equilibrium constant for the extraction process.

In this investigation it was found necessary to study the extraction at constant, but high, ionic strength. Since the extraction equilibrium constant is a function of the activities of the thallium-chloride complexes, the activity

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<sup>1</sup>Doctoral thesis number 1731, submitted November 18, 1955.

Chairman of Committee, A.F. Voigt, Department of Chemistry.

<sup>2</sup>B.A., Reed College, Portland, Oregon.

Research Assistant, Institute for Atomic Research.

coefficients and the concentrations of the various complexes need to be known, and the usual methods of determining the activity coefficients, such as simple extensions of the Debye-Huckel law, could not be used at these high values of the ionic strength. Methods and equations were developed to determine these activity coefficients. This method is applicable to systems in which the ionic strength is constant, the complex ions are large and the concentrations of the complexes are small.

It was found that the compound present in the ether phase was essentially  $\text{HTlCl}_4$  and the equilibrium constant for the extraction was defined as:

$$K = \frac{(\text{HTlCl}_4)_e}{(\text{H}^+) (\text{TlCl}_4^-)}$$

where the parentheses indicate activities and the subscript "e" indicates the ether phase. For investigations performed at constant acidity a new extraction equilibrium constant was defined:

$$K' = K(\text{H}^+) = \frac{(\text{HTlCl}_4)_e}{(\text{TlCl}_4^-)}$$

The investigation revealed that for a given constant acid concentration  $K'$  was essentially constant with varying  $\text{LiCl}$  concentrations for  $\text{LiCl}$  concentrations greater than 0.1 M. At  $\text{LiCl}$  concentrations below 0.1 M.  $K'$  increased quite markedly. This increase was believed due to the extraction of  $\text{TlCl}_3$  and/or the ionization of  $\text{HTlCl}_4$  in the ether phase at low ethereal concentrations of thallium. The extraction was dependent upon the ionic strength as shown by the change in  $K'$ , at a given acidity, with change in the value of the ionic strength. For 1.0 K.  $\text{HClO}_4$  the value of  $K'$  was 2.50 at the value of ionic strength equal to 2.0 and 5.35 at an ionic strength value equal to 3.0.

It was observed that  $K'$  was dependent upon the concentration of  $\text{HClO}_4$  to the first power. Also the over-all distribution coefficient of thallium between the aqueous and ether phases,  $K_T$ , was observed to be dependent upon the first power of the  $\text{HClO}_4$  concentration.

The true extraction equilibrium constant was:

$$K_x = \frac{(\text{HTlCl}_4)_e}{(\text{HTlCl}_4)_w}$$

Although  $K_x$  could not be directly calculated, quantities which were proportional to  $K_x$  were calculated. At  $\text{HClO}_4$  concentrations greater than 0.4 M. and  $\text{LiCl}$  concentrations greater than 0.1 M. the species extracted into isopropyl ether was shown to be  $\text{HTlCl}_4$ . At very low  $\text{LiCl}$  concentrations, below 0.05 M., the extraction was a more complicated process.

The extraction data indicated the formation of a pentachlorothallium complex. The formation constant for the complex,  $\text{TlCl}_5^{2-}$ , from thallium (III) and chloride ions was calculated to be  $3.6 \times 10^{17}$ .



SOLVENT EXTRACTION OF URSOLIC ACID AND WAX  
FROM CRANBERRY SKINS<sup>1</sup>Pong Ray Hsia<sup>2</sup>

Department of Chemical Engineering

Chemical compounds present in cranberry skins are as follows: mixed glycerides of linolenic acid, linoleic acid, oleic acid, and palmitic acid; oleic acid and arachidic acid; nonacosane and hentriacontane; and ursolic acid.

Ursolic acid is a good emulsifying agent in food and cosmetic preparations. The objective of this work was to recover ursolic acid and the other compounds, grouped together under the designation "wax", by solvent extraction.

The amount of these compounds that can be extracted from the skins by various solvents is dependent upon the nature of the solvent. Among the solvents investigated, tetrahydrofuran dissolved more than the others; ethylene dichloride and trichloroethylene were nearly equal in solvency and n-hexane dissolved the least.

The solubility of ursolic acid was determined in ethylene dichloride, trichloroethylene and tetrahydrofuran. It had a relatively high solubility in tetrahydrofuran, but the inflammability and tendency of this solvent to form peroxides limited its industrial applications. The solubility of ursolic acid in ethylene dichloride and trichloroethylene were found to be about the same.

Extraction rate investigations revealed that the compounds in the skins were difficult to extract. High temperature favored the extraction rate. At any extraction temperature, the rate curve can be broken into two sections, the falling rate section and the constant rate section. The breaking point occurs at a lower residual content when the extraction temperature is high, and vice versa. After the breaking point, extraction rate remains nearly the same regardless of extraction temperature.

Mixing investigations indicated mixing favored extraction in the region where the residual contents were relatively high. Mixing had no effect on extraction after a certain fraction of the extractable compounds had been extracted.

Pilot plant investigations of cranberry skins were conducted in the continuous countercurrent extractor of this institute. In the first series of runs, trichloroethylene was used as solvent in each run. In the second series of runs, trichloroethylene was used as solvent only in the first run. The solvent used in each of the following runs was the solution obtained from each preceding run after cooling and filtering. The third series of runs was conducted in a similar manner as the second series except ethylene dichloride was used as original solvent in place of trichloroethylene. The results indicated the yields of both ursolic acid and wax were higher in the extraction where fresh solvent was used than when the recycled solution was used. An analytical method based on infrared spectrometry was developed to determine the ursolic acid content in the extraction product.

Economical considerations indicated the thermal requirement in the extraction of cranberry skins with fresh solvent was higher than that required in the case where recycled solvent was used. The choice of the two processes mentioned therefore will be dependent, among other factors, upon the amount of product recovered, the selling price of the product, the thermal requirements in recovery of the solvent, and the overhead cost of equipment.

<sup>1</sup>Doctoral thesis number 1756, submitted December 12, 1955.

Chairman of Committee, L.K. Arnold, Department of Chemical Engineering.  
<sup>2</sup>B.S., National Central University, China. M.S., Iowa State College, Ames.  
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THE SEPTORIA DISEASE OF OATS<sup>1</sup>Marion Donald Huffman<sup>2</sup>

Department of Botany

The present investigation was undertaken to examine the Septoria disease cycle with reference to the development of each phase of the disease; and to test 4751 oat selections from the Cereal Investigations (C.I.) Collection, United States Department of Agriculture, for resistance to the disease.

Septoria disease of oats is preferred to previous names for the disease, each of which describes only one stage of the disease. All of the symptoms are caused by the same pathogen and the multiplicity of names may be confusing to one unfamiliar with the disease.

Three types of fruiting bodies of *Leptosphaeria avenaria* occurred on overwintered oat stubble. Micropycnidia producing microspores were the first to appear, occurring about the first week in April through mid-June. Perithecia appeared by the latter part of April and can be distinguished from micropycnidia by their shiny, globose appearance in contrast to the smaller, more or less linear micropycnidia. Macropycnidia producing macroconidia characteristic of Septoria formed on overwintered straw early in June and in leaf lesions from mid-June through early July. Each of the spore types collected from overwintered stubble was pathogenic on susceptible oat plants, and pure cultures of Septoria avenae were obtained from some of the isolations from the infected plants. Perithecia were not obtained in culture during this investigation, although their presence was reported in earlier work. All attempts to induce formation of the perithecia in culture failed.

Microspores and ascospores possess types of dispersal favoring wind dissemination while the cirrus formation by macropycnidia limits dissemination of macroconidia to water, or to mechanical contact of wet plants.

Microspore dissemination was measured by the operation of spore traps near areas of stubble infested with the organism. Peak dissemination dates occurred approximately two weeks prior to initial leaf symptoms in accordance with the established incubation period. Ascospores and macroconidia were not encountered during operation of the spore traps.

Although seedling infection has been reported elsewhere, it does not seem to be of any importance in Iowa, and no positive evidence of such infection was obtained. It appears that *L. avenaria* overwinters as mycelium in oat stubble, forming fruiting bodies the following spring.

Spores for use in subculturing and inoculation were obtained in abundance by the use of an oat leaf agar medium and continued transfer of spores instead of mycelium. Although macerated mycelium was as effective in causing infection as spores, the use of spores as inoculum is preferred due to their ease in application, and their similarity to natural inoculum. The use of cultural filtrate as inoculum in testing for resistance is not acceptable due to the generalized killing of the affected areas.

Although the best germination of spores occurred after at least twelve hours exposure with free water, some germination occurred after only four hours at relative humidities as low as 93.5 per cent. Seventy-five per cent germination occurred after twelve hours with free water while about five per cent germination occurred after only four hours at 93.5 per cent relative humidity.

From the C. I. Collection of 4751 oat selections, 24 were found to possess

<sup>1</sup>Doctoral thesis number 1725, submitted October 11, 1955.

Chairman of Committee, Chas. S. Reddy, Department of Botany.

<sup>2</sup>B.S., Kansas State Teachers College, Pittsburgh. M.S., Kansas State College, Manhattan. Graduate Assistant, Agricultural Experiment Station.

resistance greater than that of any commercial variety now grown in the north central United States. These selections were tested in eleven replications over a three-year period. In 1953 and 1954 only leaf spot readings were taken, while in 1955 only stem lesion readings could be taken. Leaf and stem readings were in close agreement. No immunity to the disease was found, all selections being infected to some extent. For this reason resistance should be thought of in relation to a given check variety at a given dosage of inoculum.

Resistance to L. avenaria was independent of maturity. Although many of the resistant selections are a few days later in maturity than most commercial varieties grown in Iowa, there are no evidences of escape from infection and many very susceptible selections are as late as any of the 24 resistant selections. Twenty-two of the 24 resistant selections are Victoria derivatives and are susceptible to Helminthosporium victoriae M and M. Whether resistance to L. avenaria can be derived from these selections without retaining susceptibility to H. victoriae will be a problem of extreme importance if breeding for resistance to L. avenaria is attempted.

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#### ROLE OF CARBON DIOXIDE IN THE SYNTHESIS OF AMINO ACIDS BY A PHOTOSYNTHETIC BACTERIUM IN THE DARK<sup>1</sup>

Daniel Hartz Hug<sup>2</sup>

Department of Bacteriology

Nonsulfur purple bacteria develop in the absence of light when a suitable organic substrate and atmospheric oxygen are available. The metabolism of these photosynthetic bacteria is essentially heterotrophic under these conditions. The metabolism of amino acids was investigated in Rhodospirillum rubrum, especially with regard to the role of carbon dioxide fixation in the biosynthesis of amino acids.

Carbon dioxide is required for growth on a medium containing acetate as the substrate. Nonproliferating cells do not oxidize acetate in the absence of carbon dioxide, but addition of catalytic amounts of malate will permit the oxidation to proceed. These results are evidence of the vital role of carbon dioxide in the dark-aerobic metabolism of R. rubrum.

Radioactive carbon dioxide ( $C^{14}O_2$ ) was used for tracer studies in dark-aerobic growth experiments. Radioactive carbon dioxide is fixed into many constituents of the cells. The radioactive amino acids from protein were isolated and identified by means of paper chromatography and radioautography. Aspartate, glutamate, arginine, alanine, tryptophan, proline, threonine, glycine, leucines, tyrosine, serine, methionine, valine, cystine, and lysine were labeled. Approximately half of the radioactivity in protein is found in aspartate, glutamate, alanine, and arginine.

Alanine, aspartate, and glutamate are labeled predominantly in the carboxyl groups. This labeling is consistent with a  $C_1$ - $C_2$  addition to form pyruvate,  $\beta$ -carboxylation of pyruvate to yield oxalacetate, and reactions of the citric acid cycle to yield  $\alpha$ -ketoglutarate. It is suggested that the amino acids corresponding to pyruvate, oxalacetate and  $\alpha$ -ketoglutarate are formed by transamination. The demonstrated formation of glutamate from aspartate

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<sup>1</sup>Doctoral thesis number 1776, submitted March 10, 1956.

Chairman of Committee, C. H. Werkman, Department of Bacteriology.

<sup>2</sup>B.S., Iowa State College, Ames.

Graduate Assistant, Industrial Science Research Institute.

and pyruvate in the presence of cell-free extracts is consistent with this scheme.

The amidine carbon of arginine contains 33 per cent of the activity in the molecule. The fixation of carbon dioxide by the enzyme citrulline phosphorylase is proposed to account for this observation.

Whole cells and cell-free extracts of *R. rubrum*, grown in the dark or light, contain transaminases which catalyze the formation of glutamate from  $\alpha$ -ketoglutarate and the following L-amino acids: phenylalanine, aspartate, tyrosine, ornithine, valine, leucine, isoleucine, tryptophan, histidine, and alanine. Methionine and lysine are slightly active, and  $\text{NH}_4\text{Cl}$ , proline, hydroxyproline, and glycine are ineffective as amino donors. The aspartate- $\alpha$ -ketoglutarate and phenyl-alanine- $\alpha$ -ketoglutarate reactions are reversible. Transaminases are probably involved in the biosynthesis of amino acids in *R. rubrum*.

D-glutamate-oxalacetate and D-glutamate-pyruvate transamination reactions are catalyzed by a cell-free extract. The D-amino acid transaminase activity is not caused by an L-isomer in the preparation of the D-amino acid and is not caused by glutamic acid racemase activity in the cell-free extract.

The formation of various amino acids is discussed in relation to recent studies on the biosynthesis of amino acids in microorganisms.

An air-borne radioactive material was found which caused significant errors in tracer experiments. The characteristics of the radiation were investigated and a procedure developed for avoiding errors from this source.

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## CONTAMINATION IN SEED FIELDS OF CORN RESULTING FROM INCOMPLETE DETASSELING<sup>1</sup>

Charles Dennett Hutchcroft<sup>2</sup>

Department of Agronomy

The most objectionable form of contamination in the production of hybrid corn seed is that due to self or sib pollination or pollination by a related plant within a seed field. Estimates of contamination for purposes of certification are obtained by observing the number of tassels shedding pollen when silks on the pistillate plants appear to be receptive. The minimum standards of the International Crop Improvement Association allow not more than one per cent of the ear parent stalks to have shed pollen on any one inspection. The requirement implies, though does not state, that percentage of contamination on the ear is comparable to percentage of tassels shedding pollen.

This study was initiated to investigate some of the factors involved in pollen dispersal within a corn seed production field as related to seed certification. Factors studied were date of silking, distance from source of contaminating pollen, linear length of tassel as related to percentage of contamination and the reliability of estimates of contamination measured by pollen collected on slides.

Data were collected which indicated that the effects of various levels of plants not detasseled can be measured and the relative importance of some of the factors involved in pollen dispersal can be evaluated.

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<sup>1</sup>Doctoral thesis number 1698, submitted July 12, 1955.

<sup>2</sup>Chairman of Committee, G. F. Sprague, Department of Agronomy.

<sup>2</sup>B.S., Iowa State College, Ames. M.S., *ibid*.

• Assistant Professor.

Factors over which some control can be exerted in certification requirements are distance, silking date, and the abundance of desirable pollen. Lack of control over wind and other climatic factors make it necessary to study their effects and apply a standard on the basis of an average over a period of years.

Date of silking accounted for a significant portion of the total variability in most plots when evaluated by regression analysis. The simultaneous timing of silk emergence of the pistillate parent with tassel anthesis of the intended staminate parent appeared to be of great importance in reducing contamination from any outside pollen. A requirement for control of this factor would seem desirable in the International Crop Improvement Association minimum standards.

Distance from source of contamination appeared to have a significant effect on reducing contamination when measured by regression analysis. Observations for one year, 1954, indicated contamination beyond 20 feet from the source averaged below the minimum standard for certification. Additional information is needed before conclusions can be drawn.

The amount of contamination which could be expected from a linear inch of tassel was measured in three different years. The amount of contamination per inch varied from year to year and more contamination per inch was observed as the number of inches of tassel decreased.

Vaseline-coated slides have been used in several studies to estimate levels of pollen present at a given distance from a source. The usual assumption is that expected contamination approximates the level of pollen observed. Often the slide technique is the only known method of estimating pollen dispersal. The waxy gene makes it possible to compare the usefulness of the slide method with actual contamination observed on the ear. Data obtained in this study indicated a high correlation between per cent waxy pollen on slides and waxy kernels observed. However, a comparison of the two values revealed wide differences sometimes existed. Some improvements in technique were suggested which would give more precise estimates of contamination.

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## DIMERIZATION OF VITAMIN B<sub>12a</sub><sup>1</sup>

Bruno Jaselskis<sup>2</sup>

Department of Chemistry

Solutions of vitamin B<sub>12a</sub> in water undergo changes in electrical conductivity, absorption spectrum, and pH which have puzzled workers since the isolation of the vitamin in 1949. In the present work it is shown that these changes result from the reversible union of vitamin B<sub>12a</sub> with oxygen.

The diffusion coefficients of vitamins B<sub>12</sub> and B<sub>12a</sub> have now been redetermined using a free diffusion method. The values obtained are  $2.9(1) \times 10^{-6}$  cm<sup>2</sup>/sec. for B<sub>12</sub> and  $2.3(3) \times 10^{-6}$  cm<sup>2</sup>/sec. for B<sub>12a</sub>. The molecular weights calculated from these values by the Stokes-Einstein-Longworth equation give 1380 for vitamin B<sub>12</sub> and almost twice that, 2225, for vitamin B<sub>12a</sub>. Results in agreement with these molecular weights were obtained by the Svedburg equation using values of the sedimentation coefficients (measured

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<sup>1</sup>Doctoral thesis number 1746, submitted December 7, 1955.

<sup>2</sup>Chairman of Committee, Harvey Diehl, Department of Chemistry.

<sup>2</sup>B.S., Union College, Lincoln, Nebraska. M.S., Iowa State College, Ames. Research Assistant, Industrial Science Research Institute.



for this work by Dr. H. Schachman), the diffusion coefficients, and apparent specific volumes.

The dimerization of vitamin B<sub>12a</sub> occurs after dissolution, for X-ray crystallographic evidence indicates that in the crystal the molecule is a monomer.

The apparent specific volumes of vitamins B<sub>12</sub> and B<sub>12a</sub> were measured by a sensitive synchrometric method. Erratic results obtained with B<sub>12a</sub> led to the finding that oxygen was involved. The measurements were then made with the solutions freed and also saturated with oxygen. The obtained values are:

0.665 for vitamin B<sub>12</sub> in the presence and absence of oxygen,  
 0.650 for vitamin B<sub>12a</sub> in the absence of oxygen,  
 0.713 for vitamin B<sub>12a</sub> in the presence of oxygen.

The dimerization of vitamin B<sub>12a</sub>, therefore, appeared to be caused by oxygen.

The stoichiometry of the interaction of oxygen with vitamin B<sub>12a</sub> was determined by an amperometric titration of the vitamin with a standard solution of oxygen. It was found that vitamin B<sub>12a</sub> reacts with oxygen in the ratio of two molecules of vitamin B<sub>12a</sub> to one molecule of oxygen. Solutions of vitamin B<sub>12</sub> do not react with oxygen. Reduced vitamin B<sub>12</sub>, the so-called vitamin B<sub>12r</sub>, reacts with oxygen in two steps. First, it is oxidized to vitamin B<sub>12a</sub> and then coupled to form a dimer.

The conductivity of vitamin B<sub>12a</sub> solutions was measured in the absence and in the presence of oxygen. The equivalent conductance of oxygen-free vitamin B<sub>12a</sub> solution ( $8.5 \times 10^{-4}$  M), 75, increases almost fourfold with the addition of oxygen to 306. This increase is attributed to hydroxyl ions liberated during the dimerization. The pH of solutions of vitamin B<sub>12a</sub> increases with the addition of oxygen.

Spectrophotometric measurements revealed that the spectra of oxygen-free and oxygenated solutions of vitamin B<sub>12a</sub> were almost identical but that in the spectrum of oxygenated B<sub>12a</sub> there was present a pronounced shoulder at 320 mμ not present in that of oxygen-free solution.

It was shown that B<sub>12a</sub> does not act as a catalyst in the oxidation of ferrous sulfate, potassium ferrocyanide, and sodium arsenite by air. The reduced form of methylene blue was oxidized by air in presence of B<sub>12a</sub> instantaneously.

The oxygen addition to vitamin B<sub>12a</sub> in aqueous solution follows the reaction:



FROST HEAVING, SOIL TYPE, AND SOIL WATER TENSION<sup>1</sup>Wendell Clifford Johnson<sup>2</sup>

Department of Agronomy

Frost heaving refers to the expansion of soil while freezing. It is caused mainly by an increase in moisture content and is to only a minor extent due to the expansion of pre-existing water with freezing. It is not appreciable without a capillary connection with free water, or water at zero tension. Soil heaving is important in agriculture because it results in damage to winter wheat, legumes, and certain horticultural plants such as bulbs and strawberries.

Beskow (1), a Swedish geologist, has shown that with soils of a uniform particle size:

$$Q = \frac{b^2}{(p + cb)^2} \quad (1)$$

where  $Q$  is the rate of heave or expansion of the soil in mm/hr, and  $p$  is the water tension in cm of water. The constant,  $b$ , is inversely proportional to the cube of the particle diameter. The constant,  $c$ , varies from 1.0 in silts to zero in clays. Most of the work done by Beskow and others to determine  $Q$  has been with disturbed soils of a rather coarse texture for engineering purposes.

In the present study, the rate of heave,  $Q$ , was measured over a range of water tensions using undisturbed samples taken from the upper two feet of four important soil types. These soils were the Marshall silty clay loam, Edina silty clay loam, Carrington loam, and Clarion loam.

The apparatus used consisted of a refrigerator with an inner door having a plastic window through which the expansion of freezing soil could be measured by means of an optical lever. Soil cores were frozen on porous plates connected to a water tension system by means of which the water tension could be varied from zero to 400 cm. The soil was insulated laterally with pulverized cork. The air temperature was controlled at 20°F and the temperature of the water entering the soil at 37°F.

It was learned that the rate of heave of the soils studied was not closely related to their particle size or poresize distributions. The Marshall soil heaved weakly in the top foot at tensions below 100 cm but rather strongly at the same tensions in the second foot. The Clarion and Carrington soils heaved at a moderate rate at all tensions. The Edina soil, which has long been recognized as a bad soil for frost heaving, presumably because of its claypan and poor internal drainage, was found also to have intrinsic properties in the 3-15 inch zone which would cause it to be very strongly frost heaving. The rate of heave of the claypan of the Edina is slight and per se is not the cause of the severe heave damage experienced in that soil. When all observations from the upper two feet of each soil were averaged for comparison purposes, the composite rate of heave curves for the Clarion, Carrington, and Marshall soils were very similar while the Edina showed a marked superiority in rate of heave at all tensions. Similar, except more pronounced, differences were shown in the composite curves for the 6-18 inch zone.

The regression of rate of heave,  $Q$ , on rate of water absorption,  $W$ , converted to inches of ice per hour, as measured on one soil, the Clarion, was found to be:

$$Q = .0219 + 1.024 (W - .0247) \quad (2)$$

<sup>1</sup>Doctoral thesis number 1732, submitted November 22, 1955.

Chairman of Committee, Don Kirkham, Department of Agronomy.

<sup>2</sup>A.B., University of Nebraska, Lincoln. M.S., *ibid*.

Graduate Assistant, Agricultural Experiment Station.

Evidence was obtained in support of the theory of Beskow that the main restrictions to flow of water at a given tension in a freezing soil occurs in a narrow zone adjacent to the frost line. This was done by showing that the rate of heave is independent of the geometry of the freezing soil system, and that a barrier zone below the frost line restricting half the cross sectional area of freezing soil to water flow has no effect on the rate of heave.

The effect of repeated freezing and thawing, and of wetting and drying, on a structureless soil was noted and found to first manifest itself as an increase in rate of heave at the higher tensions above 100 cm.

Treatment of a soil with a detergent and a silicone were both found to decrease the rate of heave.

#### REFERENCE

1. Beskow, Gunnar. Soil freezing and frost heaving with special application to roads and railroads. (in Swedish) Swedish Geological Society, Ser. c, No. 375, 26th Yearbook, No. 3, 1935. (English translation by J. O. Osterburg, published by Techn. Inst., Northwestern University, 1947.)

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#### RESOURCE RETURNS AND PRODUCTIVITY COEFFICIENTS FOR THE KANSAS COOPERATIVE GRAIN ELEVATOR INDUSTRY<sup>1</sup>

Paul Leo Kelley<sup>2</sup>

Department of Economics and Sociology

This study was made to determine if optimum conditions of resource use were attained in the Kansas cooperative grain elevator industry for the 1949 wheat crop year. Consumer sovereignty, the present distribution of income, and the organization of industry and primary production were assumed as given for the economic system in which the analysis was cast. Profit maximization was assumed to be the sole objective of grain elevator firms. Prices of factors and products were also assumed as given to the firm.

Specific objectives of the study were to determine:

1. Productivity coefficients for the various resource categories used in these firms.
2. Productivity differences of the various resource categories between areas and between various degrees of elevator diversification.
3. The nature of returns to scale in the various stratifications.
4. Differences between factor productivities and factor costs.
5. Recommendations for improvement in the pattern of resource use among these firms.
6. Measurements useful for comparison of economic efficiency of these firms with that of other important groups of firms in the economy.
7. Improvements that could be made in future studies of this type.

The basic data for the analysis were obtained by survey of all the Kansas cooperative grain elevators for the 1949 wheat crop year. Two hundred fifteen firms were included in the study. These firms were considered to be

<sup>1</sup>Doctoral thesis number 1784, submitted May 15, 1956. Committee Chairmen, E.O. Heady and Geoffrey Shepherd, Department of Economics and Sociology.

<sup>2</sup>B.S., Kansas State College, Manhattan. M.S., *ibid*.

a sample from a hypothetical infinite population. Inferences were restricted to physical and economic conditions approximating those prevailing in the period studied.

Data from the Kansas cooperative elevators were grouped by three risk areas, by three diversification strata, and by diversification strata within the areas. These groupings were made to determine the effects of risk and diversification on resource productivity.

Cobb-Douglas production functions of the form

$$Y = a X_1^{B_1} X_2^{B_2} X_3^{B_3}$$

were computed for each of the strata where a sufficient number of observations was available.  $Y$  was the value of the output.  $X_1$  was defined to be the value of labor services,  $X_2$  value of operating expense services, and  $X_3$  the value of capital services. Productivity coefficients and marginal products were obtained from the production functions and other basic data.

For the aggregate of 215 forms the following function was obtained:

$$Y = 4.2498 X_1^{.5201} X_2^{.0778} X_3^{.4124}$$

Marginal products for these 215 firms at the geometric means of the data were as follows: labor services -- \$1.27, operating expenses -- \$2.14, and capital services -- \$3.10.

Results from two of the diversification sorts within areas were excluded because the coefficients did not appear consistent with those obtained from the other functions and also did not appear logical from the standpoint of economic theory. Considering the above restriction, the major resource inputs were found to be allocated in an optimum fashion between area and diversification alternatives.

Evidence suggested that in general constant returns to scale prevailed for the various strata of 215 elevators in the period considered, with the exception of increasing returns to scale for a group of highly diversified plants in eastern Kansas. Decreasing returns to scale might have been in evidence if measurements had been available for management.

The productivity of capital services exceeded the cost of these services in a majority of the strata analyzed. The productivity of operating expense services, on the other hand, differed from the cost of these services in only one case out of twelve. Labor productivity was significantly greater than the cost of labor in four of the twelve functions analyzed.

The analysis of labor-capital substitution possibilities for the aggregate function and three of the area functions indicated that considerable savings could be made in certain input ranges by the use of more capital and less labor services than were used on the average.

All allocation recommendations in this study are limited by technical and labor mobility considerations. Alternatives considered are only a few of the many possible alternatives. The difficulty of obtaining precise measures of the capital and labor service inputs must be recognized.

Considering the above restrictions, resources were found to be allocated in an optimum fashion between area and diversification alternatives for the firms considered.

In future studies consideration should be given to the possibility of using other techniques of analysis such as weighted regression, linear programming, and systems of equations. Studies under different climatic and economic conditions would be useful in appraising the over-all resource problems of these firms. Of particular interest would be a consideration of total resources in the area. Also social implications of differences in labor productivity and wage rates in this industry might be appraised in the manner presented by Paul H. Douglas in his earlier works.

INHERITANCE OF STEM RUST RESISTANCE IN OATS<sup>1</sup>John Joseph Kolar<sup>2</sup>

Department of Agronomy

The investigations reported herein were undertaken to determine the mode of inheritance of stem rust resistance exhibited by several oat strains, to re-examine the interallelic relationships between genes known to condition stem rust resistance, and to determine if the variety Ukraine, when crossed with other oat strains, produced an epistatic reaction resulting in resistance to some stem rust races.

Progenies of  $F_2$  plants from 26 of the 28 possible crosses among eight oat strains, C.I. 5870 (Sac x Hajira-Joanette), R.L. 559.16 (Hajira), C.I. 6537 (Clinton x Ukraine), C.I. 6957 ([Landhafer x (Mindoo x Hajira-Joanette)] x Andrew), C.I. 3259 (Ukraine), C.I. 4024 (Canuck), C.I. 787 (Richland), and C.I. 551 (White Tartar) were tested in the  $F_3$  generation for stem rust reactions in the seedling stage to races 6, 7, 7A, and 8 at either high or low temperatures.

At low temperature, the resistance of C.I. 5870 to race 7 was conditioned by two genes while that to races 6, 7A, and 8 was conditioned by single factor pairs. At high temperature only one gene remained effective in conditioning resistance to races 7 and 7A. This strain was concluded to possess the Richland and Hajira factors, the A, B, and C genes.

Tests of crosses involving R.L. 559.16 revealed its reaction to stem rust was controlled by the same factors operative in C.I. 5870. Thus, its genotype in reference to stem rust resistance was also considered to be ABC.

Single factors governed the resistance of C.I. 6537 to races 6 and 7 while two factors determined its resistance to race 8 at low temperature. Only one factor remained effective in conditioning resistance to race 8 at high temperature. Results suggested that reaction of C.I. 6537 was conditioned by the B, C, and D genes, or the Hajira and White Tartar factors.

C.I. 6957 contributed two types of resistance to progenies of crosses in which it was involved, thus indicating that it was heterogeneous for rust reaction. Some crosses derived the Richland, White Tartar, and Hajira factors which provided two genes conditioning reaction to races 7 and 8, and single genes conditioning reaction to races 6 and 7A at low temperature. Only the Richland and White Tartar genes were obtained by progenies of other crosses, thereby providing resistance at all temperatures to races 7, 7A, and 8.

The independence of inheritance of the Hajira resistance was demonstrated in this series of crosses. The Hajira factors for stem rust resistance were readily combined with either the Richland or White Tartar genes or with both in crosses where these genes were linked in the coupling phase.

No resistance to any race was contributed by C.I. 3259 to progenies of the five crosses in which it was used as a parent. Observed reactions to stem rust were in harmony with the postulated genotypes of the other parents of these crosses.

<sup>1</sup>Doctoral thesis number 1744, submitted December 6, 1955. Chairmen of Committee, K. J. Frey and I. J. Johnson, Department of Agronomy.

<sup>2</sup>B.S., Montana State College, Bozeman. M.S., *ibid*.

Graduate Assistant, Agricultural Experiment Station.



AN APPRAISAL OF THE PUBLIC JUNIOR COLLEGES OF IOWA<sup>1</sup>Virgil Seth Lagomarcino<sup>2</sup>

Department of Vocational Education

This study was designed to provide a basis for a better understanding of the status of the junior college movement in the nation in general, and in Iowa in particular. Specifically, the purposes of this study were:

1. To analyze the historical background and philosophy of the junior college movement.
2. To trace the development of the public junior colleges in Iowa.
3. To appraise certain aspects of the present 16 public junior colleges in Iowa.
4. To predict the scholastic achievement of the two-year graduates of Iowa public junior colleges who matriculated at the State University of Iowa, the Iowa State College, and the Iowa State Teachers College in the fall terms of 1951 and 1952.

Although the first public junior college in Iowa was founded at Mason City in 1918, it was not until 1923 that the Iowa Legislative Assembly officially reorganized the public junior college in the state. The purpose of this legislation was not to legalize the five junior colleges then in existence, but rather to legalize the payment of tuition. The first specific reference in the statutes of Iowa pertaining to public junior colleges was an act in 1927 which legalized the public junior college as part of the public school system.

Public junior colleges in Iowa were accredited prior to 1927 by the Iowa Intercollegiate Standing Committee. During the period from 1927 to 1941, the Intercollegiate Standing Committee worked with the State Department of Public Instruction in approving the public junior colleges of Iowa. Since 1941 the State Department of Public Instruction has exercised full responsibility for the standards and for the approval of the public junior colleges.

In the period from the establishment of the first public junior college in Iowa (Mason City, 1918) to the establishment of the latest public junior college (Keokuk, 1953), a total of 35 such institutions have been formed. Of this number, 19 have been discontinued, leaving a total as of April 1, 1955, of 16 public junior colleges in operation.

A total of 8128 students have been graduated from the 16 public junior colleges which were in operation in 1954-1955. The enrollments have ranged from a low of 431 in 1944-1945, when only 12 public junior colleges were open, to a high of 2433, when 27 institutions were in operation. Only 46.5 per cent of the total number of freshmen who enrolled in the years between 1944-1950 and 1952-1953, continued into the sophomore year.

The public junior college in Iowa has been essentially a college preparatory institution. In 1954-1955 the 16 public junior colleges offered a total of 2629 semester hours of academic instruction. The greatest number of semester hours were offered in the science curricula (551) and in the social sciences (399). A total of 576 different courses were offered in the 16 schools.

A total of 855 different classes operated in the public junior colleges of the state in the 1954-1955 school year. One hundred classes enrolled 5 or fewer students (11.7 per cent). Approximately one-half of the classes (424 or 49.5 per cent) had a membership of 15 or fewer students.

<sup>1</sup>Doctoral thesis number 1704, submitted July 29, 1955. Chairman of Committee, Barton Morgan, Department of Vocational Education.

<sup>2</sup>B.A., Coe College, Cedar Rapids, Iowa. M.S.E., Drake University, Des Moines, Iowa. Graduate Assistant, Vocational Education.

A total of 297 instructors taught in the public junior colleges in 1954-1955. Of this number 63.6 per cent were men and 36.4 per cent were women. A total of 232 teachers (78.1 per cent) held the Master's degree and 64 held the Bachelor's degree. In all, 230, or 77.4 per cent of the junior college instructors, taught in their major fields. Only 52 instructors were assigned full-time teaching loads in the junior college. In 1954-1955 a total of 22 teachers (7.4 per cent) were temporarily approved by the Director of Junior Colleges, to teach on less than the basic standards.

Involved in the prediction of academic success of the two-year junior college transfer were three objectives: 1) to predict the grade point of a two-year public junior college student who matriculated at one of the three state institutions of higher learning, 2) to predict the chances out of 100 that a two-year transfer from a public junior college would have of being graduated when he enrolled at one of the three state institutions, 3) to predict the probability of his being graduated in the upper half of his class at each of the three state institutions.

The prediction variables used in these analyses were the student's high school academic average and the academic average earned in the junior college. These were used as prediction variables because they were the only data available for all 257 students.

The data for this investigation were collected from the Office of the Registrar at each of the three state institutions of higher learning and from the Deans of each of the 15 junior colleges which had graduated students during the period studied.

It was assumed for purposes of this study that a student was classified in the attrition group if he were neither graduated nor enrolled in one of the three institutions at the end of a two-year period following his transfer. It was further assumed that the period from 1950 through 1952 was a sufficient length of time in which to evaluate the success of junior college transfer students.

Four delimitations were imposed in this study. These were in relation to students who

1. Transferred from the public junior colleges in Iowa to the State University of Iowa, the Iowa State College, and the Iowa State Teachers College in the fall terms of 1950, 1951, and 1952.
2. Had graduated from one of the 16 public junior colleges.
3. Had graduated from junior college in the year immediately preceding the transfer.
4. Had transferred directly to one of the three state institutions of higher learning and continued to be enrolled there. No subsequent transfer to any of the three state institutions was considered.

A total of 257 junior college graduates who matriculated in the three state institutions in the period were studied. The academic averages of these students in high school, junior college, and in senior college constituted the raw data for analysis. The statistical techniques used in the treatment of these data were analysis of regression, biserial correlation, and discriminant analysis.

Each of the students studied was a transfer from a public junior college in existence at the time the study was made. Several students who had transferred from defunct junior colleges were enrolled at each state institution. These students were dropped from this study, since this investigation sought to appraise only those public junior colleges which were in operation at the time the study was made.

It was found that out of a total of 257 students who had transferred to the State University of Iowa, the Iowa State College, and the Iowa State Teachers College, a total of 175 had survived. Of these, 160 had been graduated and

15 were still enrolled. Ten of the latter were in attendance at Iowa State College. Current enrollees were classified as survivors because 1) they had not discontinued their studies, and 2) not all nontransfers originally enrolling in these three senior colleges graduate in a four-year period.

The attrition of junior college transfers was greatest at the Iowa State College in which there were 28 students (39.4 per cent) who failed to survive out of a total of 71 who matriculated. The percentage of attrition was somewhat less at the State University of Iowa (31.3 per cent) in which 87 survived of the 127 who had transferred. The percentage of attrition was smallest at the Iowa State Teachers College (23.7 per cent) in which 14 students out of a total transfer group of 59 failed to survive.

When an investigation was made of the tendency to be graduated the analysis of regression was used to determine the prediction equation. It was found in the development of this equation that the high school average could be dropped as a prediction variable.

The following were found to be the most probable predictions.

When the junior college average was 2.00, the predicted grade point was:

SUI, 1.583; ISC, 1.436; ISTC, 1.528.

When the junior college average was 3.00, the predicted grade point was:

SUI, 2.322; ISC, 2.175; ISTC, 2.267.

When the junior college average was 4.00, the predicted grade point was:

SUI, 3.061; ISC, 2.914; ISTC, 3.006.

From a computation of the standard error of estimate it was found that 50 per cent of the students could be expected to make grade point averages between .383 above and .383 below these predictions.

With the use of the discriminant analysis the probability of graduation from each of the three state institutions was computed. The high school average was not found to be significant as a prediction variable and was dropped. The biserial correlation when junior college grades only were used to predict graduation tendency was .3002.

When the probability of graduation was predicted for transfer students it was found that a student who had a 2.0 average in junior college had 60 chances in 100 to be graduated from the State University of Iowa, 53 chances in 100 to be graduated from the Iowa State College, and 70 chances in 100 to be graduated from Iowa State Teachers College. The student with a 3.0 average had 71 chances in 100 to be graduated at SUI, 65 chances in 100 at ISC, and 80 chances in 100 at ISTC.

Lastly, when the prediction was made of the tendency to be graduated above the median at each institution, it was found that a junior college transfer with a 2.0 grade point had 13 chances in 100 at SUI, 17 chances in 100 at ISC, and 23 chances in 100 at ISTC. If a student had a 3.0 average in junior college his chances at SUI were 32; at ISC, 38; and at ISTC, 47.

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PROBLEMS AND IMPLICATIONS OF INTRAFAMILY FARM PROPERTY  
TRANSFERS IN GRUNDY COUNTY, IOWA<sup>1</sup>Buel Franklin Lanpher, Jr.<sup>2</sup>

Department of Economics and Sociology

The objective of this study was to assist owners of land in finding solutions to the problems they experience in attempting to achieve an optimum of their goals associated with the intrafamily transfer of farm property. As guides for carrying out this inquiry, hypotheses were formulated as to the specific problems that landowners have in achieving transfer objectives, the causes of these problems, and some of the possible means of solving the problems. In attempting to test these hypotheses, empirical data were obtained from interviews with owners of land in Grundy County and from courthouse records in Grundy County. This county was chosen for the geographic source of data because it is relatively free of urban influences and because the soil resources and type of farming appeared to be similar to much of the Northern Cornbelt. Information was obtained from a random sample of 76 landowners. From 45 of these landowners, information was obtained about the property transfers of deceased relatives. Data were also gathered from courthouse records in regard to these 45 deceased relatives. In addition, limited data from courthouse records were obtained concerning 172 landowners who died between January 1, 1948 and July 1, 1954.

In seeking achievement of their transfer objectives, 51 of the 76 landowners who were interviewed had made a definite transfer plan other than that of being satisfied with the law of descent and distribution. Of the 51 respondents with plans, 42 had made a will and nine more had a definite plan which they intended to put into written form. Ten respondents intended to make a definite plan, and 15 felt that they would be satisfied with an intestate distribution of their property. Sixty-seven per cent of the 45 deceased relatives had made a will as had 63 per cent of the 172 landowners who died in the 1948-54 period.

Farm owners had considerable difficulty stating what goals they wanted to achieve in the transfer process. The average number of objectives volunteered per respondent was .88 of an objective. However, the average number of objectives pointed out by the respondents when shown a prepared list of objectives was 5.29, and the respondents indicated that the deceased relatives had had an average of 5.67 transfer objectives. The specific transfer goals and the percentage of respondents having each goal were as follows: retirement income, 100 per cent; equitable treatment of children, 100 per cent; early assistance to children, 95 per cent; minimize transfer costs and taxes, 95 per cent; keep the farm in the family, 64 per cent; prevent the division of land into uneconomic sized units, 43 per cent; prevent one of the heirs from acquiring an overburdensome debt, 40 per cent; and, prevent the breakup of the going concern, 37 per cent.

The respondents who had made a definite transfer plan appeared to be more aware of what they wanted to achieve than did the respondents who had not made any transfer plan. An average of twice as many transfer objectives was voluntarily stated by the respondents who had transfer plans while the average number of objectives given by each group after seeing the prepared list was almost identical.

The average net worth of the respondent landowners was about \$70,000

<sup>1</sup>Doctoral thesis number 1730, submitted November 17, 1955. Chairman of Committee, John F. Timmons, Department of Economics and Sociology.

<sup>2</sup>B.S., University of Missouri, Columbia. M.A., *ibid*. Associate, Agricultural Experiment Station.

and an average of 167 acres of land was owned. The landowners who died in the 1948-54 period had an average net worth of about \$60,000, and they owned an average of 175 acres of land.

The empirical data indicated that the intrafamily transfer objectives of the deceased relatives were largely achieved in the majority of the cases except possibly for the objective of minimizing costs and taxes. This success in most instances did not appear to be the result of definite steps taken or plans made by deceased relatives. In most cases, the heirs expressed satisfaction with the combined inter vivos and death transfers of deceased relatives and also appeared to have come to an amicable settlement of the estates. In those cases where transfer objectives such as failing to prevent overburdensome debt were not achieved, serious problems were experienced by the heirs.

The data obtained in this study suggested that the respondent landowners may fail, or that there were potential dangers which may cause them to fail, to achieve their transfer goals in a large share of the cases. In respect to the goal of securing adequate retirement income the accumulated capital of the respondent and spouse (if any) was found to be insufficient in two-thirds of the cases using \$4,000 as an acceptable yearly income and five per cent return on capital. An even greater insufficiency of retirement income would occur if the respondent decided to use part of his resources to achieve the competing objectives of giving early assistance to children or to make inter vivos gifts in order to minimize costs and taxes.

Another large area of conflict between objectives was found to exist between the objective of equitable treatment of children and the group of more or less complementary objectives of protecting the going concern, preventing overburdensome debt, preventing the division of land into inefficient units, and keeping the farm in the family. This study found evidence that the respondents in the majority of the cases had not made transfer plans which would result in an equal treatment of their children from a monetary standpoint when inter vivos plus potential death transfers were considered. In regard to the group of complementary objectives very few of the respondents with transfer plans had included provisions which would effectively enable their achievement. One of the main obstacles to making such provisions was the respondents' fear that some of the children might consider that inequitable treatment would be given. Furthermore, respondents appeared to have misconceptions as to the extent that specific specifications in their transfer plans would serve to achieve transfer objectives. The making of a will, regardless of its provisions, was commonly considered by the respondents as a method of reducing costs and taxes, although no evidence was found to support this. On the contrary, there was some evidence from the cases of landowners dying in the 1948-54 period that such costs as court costs and lawyer fees might tend to be higher for testate cases than for intestate cases.

The data from the 1948-54 period indicated that each of the various types of costs and taxes in estate settlement varied with the gross value of property. A regression calculation found that lawyer fees tended to increase by \$1.55 for each \$100 of gross value. By regression analysis it was also estimated that in similar situations the total costs in 95 per cent of the cases would not exceed \$1194 plus \$4.46 for each \$100 of gross value. Exemptions allowed under the federal estate tax and the Iowa inheritance tax according to the manner of distribution resulted in no tax liability for one-half of the estates settled in the 1948-54 period.

In conclusion, the ownership of land in Grundy County appeared to be significantly related to the intrafamily transfer of property. Economic assistance involving gifts or an economic opportunity had been received by every member of a sample of 76 landowners. However, the respondents had misconceptions and lack of knowledge of methods that might be used to assist in achieving transfer objectives, and thus, remedial action appears to be primarily a matter of providing information through an educational program.



PRENATAL MORTALITY IN SWINE<sup>1</sup>Earl Loren Lasley<sup>2</sup>

Departments of Animal Husbandry and of Genetics

Reproductive performance of a breeding herd which initially numbered 201 gilts is summarized. Purebred Landrace, purebred Poland China and four crossbred groups were included. Females that failed to farrow, following periods of pen mating, were rebred and slaughtered to evaluate cause of reproductive failure. Sows that farrowed two litters were rebred for a third and slaughtered during gestation. The average stage of gestation for sows slaughtered was 75 days.

Only 75 per cent of 192 gilts farrowed when pen mated (about ten gilts per boar) for six weeks even though 94 per cent were later found to be capable of reproduction. Seventy-two per cent of 137 first litter sows farrowed when pen mated for six weeks. Ninety-six per cent were capable of reproduction, as indicated by subsequent performance. Ninety-five per cent of the second litter sows were pregnant when slaughtered. In this instance sows were penned with four boars in a single lot. Major causes of infertility were believed to be the pen mating method of breeding, age of boars and gilts, and boar infertility.

Complete records (two litters farrowed and one examined at slaughter) were obtained for 87 sows. The average number of corpora lutea formed was 16.4. The average litter sizes for the first, second, and slaughter litters were 9.4, 11.2, and 9.7, respectively. Although litter size of the various groups was nearly identical at slaughter, Poland China gilts and first litter sows produced significantly smaller litters than those of other breeding groups. Per cent mortality of ova from maturation to 75 days was 39 per cent for the 87 sows that had complete reproductive records.

Heritability, computed as paternal half-sister correlation, was 10 per cent for number of corpora lutea, zero for size of first litter, 8 per cent for size of second litter, and 5 per cent for size of slaughter litter. In each instance the heritability value was smaller than the appropriate standard error. Repeatabilities were 0.15 between first and second litters, 0.10 between second and third litters, and -0.06 between first and third litters.

Maternal influence was present for number of corpora lutea and litter size. Genetic factors and maternal influence were persistent in their effects for different litters. A negative environmental correlation between sizes of second and size of slaughter litter suggested that factors peculiar to individuals which caused them to produce a large litter in one season favored production of a small litter in the next.

The average per cent prenatal mortality was 40.1 for all sows slaughtered in the final phase. Dead or degenerating fetuses accounted for 5.1 per cent of the corpora lutea. Estimates of per cent mortality tended to be lower when made at advanced stages of gestation. Failure to recognize complete mortality of some litters early in gestation was responsible for reduced mortality estimates in later stages of gestation. There was little evidence of real differences in per cent mortality among breeding groups. Per cent mortality was also consistent for sows slaughtered in different seasons. Heritability of per cent mortality was 38 per cent. The fact that the sire component of variance was slightly greater than the dam component suggested that some loci causing mortality were sex-linked.

<sup>1</sup>Doctoral thesis number 1729, submitted November 14, 1955.

Chairmen of Committee, L.H. Hazel, Department of Animal Husbandry, and John W. Gowen, Department of Genetics.

<sup>2</sup>B.S., North Dakota Agricultural College, Fargo. M.S., *ibid*.

There was no evidence of increased mortality due to greater intra-uterine competition as the number of ova shed increased.

The presence of dead fetuses at an advanced stage of gestation was largely associated with particular sires and dams. Late death losses appeared to affect differentially litters that implanted higher than average numbers of embryos and tended to equalize final litter size.

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### QUALITATIVE AND QUANTITATIVE STUDIES ON PROTEOLYTIC DIGESTIVE ENZYMES IN BABY PIG NUTRITION<sup>1</sup>

Charles John Lewis<sup>2</sup>

Department of Animal Husbandry

Ten experiments involving 455 pigs were conducted to determine the adequacy of the proteolytic digestive enzymes of the baby pig with particular reference to the utilization of soybean protein. The problem was approached from four general avenues: the supplementation of various proteolytic digestive enzymes to baby pig diets; the feeding of soybean protein hydrolysates; analysis of secretory tissue for enzyme activity; and the determination of the digestion coefficients of the soybean protein in the presence or absence of added proteolytic enzymes.

In all experiments, baby pigs of about 5.5 to 6.5 pounds body weight and 7 to 10 days of age were weaned directly to the experimental diets. In all cases the diets were fed dry. The experimental periods were four weeks in duration.

The inclusion of 40 per cent dried skim milk in an otherwise semi-purified soybean protein diet resulted in marked improvements in pig gains and feed efficiency. Part of this improvement in pig performance, due to dried skim milk, was found to be due to the lactose fraction. By including lactose and casein (equivalent to the carbohydrate and protein supplied by 40 per cent dried skim milk) in the purified soybean protein diet, pig performance could be produced that was comparable to that obtained by the addition of 40 per cent dried skim milk.

Several commercial sources of purified soybean proteins were compared in baby pig diets. Growth and feed efficiency data revealed marked differences among the protein sources. However, all of the soybean proteins (which were supplemented with methionine) were inferior to dried skim milk as sources of protein for the baby pig.

The addition of 1 per cent pepsin, pancreatin, papain, or Mycozyme to Drackett C-1 assay protein-lactose diets of pigs fed in groups resulted in improved growth and feed efficiency. For example, the average effect of adding 1 per cent papsin (1:3000) was to improve baby pig gains 16 per cent and improve feed efficiency 6.5 per cent. The addition of 0.5 per cent Star-Zyme P failed to improve growth. The combination of pepsin and pancreatin appeared to be superior to either when fed alone. The feeding of crystalline pepsin resulted in erratic responses, but, when fed to pigs fed in groups, a good response in gain was obtained, particularly at an early age. In one experiment the addition of 1 per cent pepsin plus 1 per cent pancreatin to a

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<sup>1</sup>Doctoral thesis number 1799, submitted May 31, 1956.

Chairman of Committee, Damon Catron, Department of Animal Husbandry.

<sup>2</sup>B.S., Utah State Agricultural College, Logan. M.S., Iowa State College, Ames. Graduate Assistant, Agricultural Experiment Station.

soybean protein casein-lactose diet resulted in improved pig gains and feed efficiency. The most consistent response to proteolytic enzyme supplementation was observed in the presence of fecal looseness or mild baby-pig scours.

The addition of proteolytic enzymes to the diets of pigs that were 53 days of age (28 pounds) failed to improve growth.

The addition of proteolytic enzymes to the same type of diet of pigs reared individually in a relatively disease-free building failed to produce any consistent improvement in gains and feed efficiency. The reason for the lack of response in this building was discussed. Pigs reared individually in the relatively disease-free unit were about 5 pounds heavier at five weeks of age than pigs fed identical diets in groups in conventional type experimental buildings. Pigs reared individually on wire grew as well as pigs reared individually on the floor. There was no difference in response to crude pepsin supplementation whether the pigs were reared on the wire or on the floor.

The enzymatic predigestion of solvent soybean oil meal (50 per cent protein) or Drackett C-1 assay protein with pancreatin resulted in improved pig growth and feed utilization when fed to baby pigs. In general, and within the extent of predigestion carried out, increasing the extent of hydrolysis of the proteins resulted in corresponding improvements in pigs gains and feed conversion ratios.

Extracts of the stomachs and pancreases of pigs sacrificed at weekly intervals from birth to six weeks of age revealed that pepsin activity was low at birth and increased markedly with age. Proteolytic activity of the pancreas was quite variable and there was no definite trend toward increasing activity with age.

The results of the digestibility studies were highly variable. Although there was a trend toward increasing digestibility of the soybean protein with increasing age, the variability was too great to allow definite conclusions either with regard to age or treatments. Improvements in the techniques employed to conduct the digestibility studies were indicated.

The blood hemoglobin concentrations of the pigs were not affected by the pepsin supplementation.

The possibility that the response from crude enzyme preparations could have been due to some factor(s) other than enzymes was recognized and discussed.

The improved pig performance resulting from proteolytic enzyme supplementation, the results of the analysis of the digestive secretory tissue, and the marked increase in gains and feed efficiency of the pigs fed the soybean protein hydrolysates indicated that the baby pig does not secrete sufficient quantities of proteolytic digestive enzymes and/or does not have the digestive capacity to adequately utilize soybean protein.

The immediate need for further research was discussed.

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OPTIMUM FARM PLANS FOR BEGINNING FARMERS IN CENTRAL IOWA  
AN APPLICATION OF LINEAR PROGRAMMING<sup>1</sup>Arthur Buren Mackie<sup>2</sup>

Department of Economics and Sociology

The specific objective of this study was to determine farm plans which best fit the resources of beginning farmers who are tenants on crop-share rented farms in central Iowa. To accomplish this objective, optimum plans were computed for various capital and management situations by use of the linear programming technique. This procedure was followed since quite different recommendations appeared appropriate for tenants with different managerial abilities and different resource supplies. In computing optimum plans, consideration was given to the nature of all limiting resources including land, labor, feed, buildings, capital, and managerial ability.

Where all enterprises competed freely for the use of resources, the effect of management on enterprise combinations depended upon capital availability. When capital was limited to \$3000, managerial ability in livestock production had no effect on the selection of enterprises and the most profitable farm plan included a corn-corn-soybean rotation with fertilization and the grain sold for cash. Use of all funds for crop production and fertilization gave greater profits when capital was very limited. Some fertilization of crops was always more profitable than investment in livestock. Livestock did not become profitable until \$5000 of capital was available. When management was at average levels for all enterprises, optimum plans then included spring hogs with the above rotation partially replaced by a corn-soybean-corn-meadow rotation to provide forage. As capital was increased beyond \$5000, a spring hog enterprise was included until hog building space became limitational. This situation held true for all management situations, except when the tenant was above average only in dairying. Fall hogs, feeder cattle, and poultry became profitable investment opportunities only when capital was increased beyond \$10,000. With this amount of capital, the enterprises included in the optimum plans were related to the nature of all limiting resources and the level of livestock management. Dairying was included in the plan only when management was above average for this enterprise but was at average levels for all other enterprises. Spring and fall hogs and poultry were included in all optimum plans at high capital levels, regardless of the level of livestock management considered.

To consider a wider range of planning situations, optimum plans also were computed which involve diversified livestock programs resulting from reductions in the most profitable enterprise (spring hogs) either by a building limitation or by risk aversion. When the size of the hog enterprise was limited to 13 litters by building space, the optimum combination of enterprises varied with the level of livestock management. Adding high forage consuming livestock to the farm plan resulted in a higher proportion of the land being planted to meadow. Placing a limitation on the size of the spring hog enterprise reduced profits as much as 39 per cent for one situation; for other situations the reduction in profits was less. Profits were only slightly reduced for the situation with above-average management for the dairy enterprise and all other enterprises with average management. Diversification reduced profits more with average management for all activities than with above-average management for all activities. Similar net income reductions were obtained

<sup>1</sup>Doctoral thesis number 1809, submitted June 4, 1956. Chairman of Committee, Earl O. Heady, Department of Economics and Sociology.

<sup>2</sup>B.S., North Carolina State College, Raleigh. M.S., *ibid.*  
Associate, Agricultural Extension Service.

for all management situations where all plans contained at least 10 dairy cows, 200 hens, and a two-litter hog system. Diversification to meet risks lowers farm profits; however, many beginning farmers with small amounts of capital or low equity will prefer less profit, as long as it lowers risks.

Plans were computed also for 1954 and 1955 hog prices because variation in product prices influences the most profitable combination of crops and livestock. These plans indicated that when hog prices fall in relation to other livestock prices, feeder cattle and dairying become relatively more profitable than spring hogs when management was average. Improved feeding efficiency tended to offset part of the effects of lower hog prices. Consequently, the need for diversification of livestock enterprises to guard against price uncertainty was greater for beginning farmers with average management. Improvement of managerial ability should increase income and also enhance the ability of young farmers to withstand periods of unfavorable prices.

Some plans were computed also for above-average crop management. These plans indicated that the selection of the most profitable combinations of crops and livestock was not affected by the level of crop management; only profits were increased. Crop management does not alter the basic recommendations that are appropriate for beginning farmers.

A universal recommendation would not be appropriate for all farmers. In several capital and management situations, especially at high capital levels, several almost equally profitable plans were obtained. When farmers have a number of alternative plans from which to choose, the degree of flexibility of farm organization is increased, thereby making possible greater short-run enterprise adjustments to changing product prices. Beginning farmers should plan, therefore, according to their own managerial abilities, farm conditions, and resource supplies, if they wish to maximize profits. No one farm plan is best for all farmers on the same soil type and with the same management ability and resource limitations. The most profitable organization of enterprises, or allocation of resources, for beginning farmers depends on 1) existing price relationships, 2) availability of capital, labor, and livestock housing, 3) managerial ability, and 4) the input-output relationships for crop and livestock enterprises considered.

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#### REPEATABILITY AND HERITABILITY OF BIRTH, WEANING, AND SHEARLING WEIGHTS AMONG RANGE SHEEP IN CANADA<sup>1</sup>

William Norman MacNaughton<sup>2</sup>

Department of Animal Husbandry

Records on over 5000 Rambouillet and Canadian Corriedale lambs raised in the flock of the Experimental Farm, Lethbridge, Alberta, Canada, during the years 1936 to 1952, were analyzed with regard to birth, weaning, and shearling weights. Constants representing the fixed effects of environment including sex, age of dam, type of girth, and age at weaning were calculated for the birth and weaning data. The heritability, repeatability, and phenotypic and genetic correlations of these traits were estimated for each breed.

The birth and weaning data were adjusted by means of these constants to correct for the effects of identifiable environmental factors. Shearling weights

<sup>1</sup>Doctoral thesis number 1763, submitted February 23, 1956.

Chairman of Committee, Jay L. Lush, Department of Animal Husbandry.

<sup>2</sup>B.Sc., University of Alberta, Edmonton, Canada. M.Sc., *ibid*.



were used in their raw state. Adjustments for sex and for type of birth were applied to the birth data of both breeds. For Canadian Corriedale lambs, adjustment of birth weight for age of dam was necessary only for those from two-year-old dams. The weaning data were corrected for the effects of sex, age of dam, type of birth and rearing, and age at weaning. The adjustments for the various environmental factors, so as to bring the weights to the basis of females born singly to mature dams and, in the case of weaning weight, to a standard age of 170 days at weaning, were:

Factor		Rambouillet		Canadian Corriedale	
		Birth lbs.	Weaning lbs.	Birth lbs.	Weaning lbs.
Sex	Male	-0.61	-5.4	-0.48	-5.3
	Wether		-3.1		-3.2
	Female	---	---	---	---
Age of dam	2 years	---	8.8	0.48	4.9
	3 years	---	3.0	---	2.1
	4-5-6 years	---	---	---	---
	Aged	---	2.1	---	5.0
Type of birth and rearing	Twin r. twin	1.95	14.7	1.78	9.5
	Twin r. singly	---	4.5	---	0.4
	Single	---	---	---	---
Age at weaning per day			0.462		0.389

The adjustments required for age of dam indicate that the Canadian Corriedale ewes reached maturity more rapidly than Rambouillets but were unable to maintain high productivity for as long a period.

Heritabilities were calculated by the intrayear intrasire regression of offspring on dam. All estimates were generally high. Heritability of birth weight was 0.27 in the Rambouillet and 0.36 in the Canadian Corriedale. Corresponding estimates for weaning weight were 0.33 in the Rambouillet and 0.45 for the Canadian Corriedales while those for shearling weight were 0.52 and 0.46 for Rambouillets and Canadian Corriedales, respectively.

An intragroup analysis, in which each group contained contemporary ewes with the same number of records produced in the same sequence of years, was used for estimating repeatability. The correlation between birth weights of lambs born from the same ewe was 0.27 in Rambouillets and 0.36 in Canadian Corriedales. The corresponding correlations for weaning weight in Rambouillets and Canadian Corriedale ewes were 0.25 and 0.30, respectively.

Phenotypic correlations between one body weight and another on the same sheep were high, ranging from 0.40 to 0.61. Listed in order for Rambouillet and Canadian Corriedale sheep, they were 0.40 and 0.52 between birth and weaning weight, 0.36 and 0.37 between birth and shearling weight, and 0.46 and 0.61 between weaning and shearling weight.

Genetic correlations between birth and weaning weight were 0.24 in the Rambouillet and 0.54 in the Canadian Corriedale breed. The genetic correlations between birth and shearling weight were 0.44 in the Rambouillets and 0.50 in the Canadian Corriedales while the corresponding correlations between weaning and shearling weight in the Rambouillets and Canadian Corriedales were 0.06 and 0.06, respectively.

The genetic correlations between birth and shearling weight were high

while those between weaning and shearling weight were low. The possibility of a systematic bias causing the weaning-shearling correlation to be low was examined. A tendency toward a negative correlation between type of birth of the unadjusted shearling observations and the type of birth which caused a specific adjustment in the dams was found. This tendency would have reduced the covariances between the adjusted weaning weights and the unadjusted shearling weights, causing the estimated correlation to be too low.

The apparent consequences of the methods of selection being followed were reviewed. The most satisfactory method of selection to achieve improvement in the economic characteristics of sheep appears to be by the use of selection indexes for selection at weanling and shearling age.

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### PHYSIOLOGICAL STIMULATION OF OOSPORE FORMATION BETWEEN *PYTHIUM* SPECIES<sup>1</sup>

Harold Stanley MacWithey, Jr.<sup>2</sup>

Department of Botany

Investigations of interaction between microorganisms with respect to stimulation of formation of sex structures have occupied many research workers. Studies of such interactions in the *Pythiaceae* have been restricted to investigation of stimulation in *Phytophthora*. Following the discovery of stimulation in dual cultures of *Phytophthora* in 1922, similar behavior was described in other members of the genus but investigation of the neighboring genus *Pythium* along similar lines has not been forthcoming. In 1943 and 1946 interspecific pairings of a variety of *Pythium* species showed an interculture antagonism and parasitism, but stimulation of sex structures in such combinations was absent.

The isolation of two sterile *Pythium* species from diseased corn root, which showed stimulation of sex structures when grown in matched culture, afforded an opportunity for study of interaction as it was related to sexuality in this genus. The work was begun in the winter of 1951-1952 and demonstration of a dialyzable stimulatory substance active in inducing the formation of sex structures suggested investigation of the production and assay of filtrates and extracts of the stimulatory organism.

In both dual and dialysis membrane-separated cultures of the two isolates, "A" and "B", stimulation of sex structures was shown to take place concurrently with mutual inhibition of growth and pathogenesis of isolate "B". The effect of certain environmental conditions, temperature, reaction of the medium, carbohydrate and nitrogen nutrients, vitamins, and age of cultures was investigated in single, dual, and membrane-separated cultures.

Temperature studies showed an optimum range in which the "B" culture was most receptive to stimulation and in which the stimulatory "A" culture showed its greatest activity. The temperature at which "B" was most receptive to stimulation was identical to that temperature at which stimulation was most abundant in dual culture. With respect to "A" culture optimum growth of the culture induced a corresponding optimum stimulation of sex structures. At the maximum temperature for growth and above, the capacity of "A" culture for stimulation was destroyed.

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<sup>1</sup>Doctoral thesis number 1769, submitted May 6, 1956.

Chairman of Committee, Joseph C. Gilman, Department of Botany.

<sup>2</sup>B.S., Northwestern University, Evanston, Illinois. Graduate Assistant.

Culture media adjusted to alkaline reaction permitted more extensive association of the mycelium and stimulation of sex structures in dual culture. Under acid conditions association was less extensive, and pathogenesis and stimulation correspondingly reduced.

Addition of carbohydrates to culture medium increased the extent of association in dual culture, and, depending upon the type and concentration of the carbohydrate, enhanced or depressed stimulation and pathogenesis. Media containing raffinose or sucrose on which the growth rates of the isolates were identical and more rapid than the unsupplemented check, produced opposite behavior with respect to stimulation and pathogenesis in dual culture. On a medium containing ribose the growth rate was depressed but stimulation and pathogenesis in dual culture was enhanced. Other carbohydrates were intermediate in their effect on growth and stimulation.

Addition of nitrogen nutrients to the culture medium in most cases decreased association, stimulation, and pathogenesis. Of twenty amino acids added singly to the culture medium, four caused an increase in stimulation over the untreated medium. The remaining amino acids either depressed or prevented stimulation, association, and pathogenesis.

Supplementing the culture medium with a number of vitamin preparations gave no detectable increase in stimulation in dual culture. Cultures "A" and "B" were shown to be heterotrophic for thiamin when grown on a glucose-asparagine medium.

Membrane-matings of cultures "A" and "B", one to five days old, demonstrated an increase in the capacity of "A" to stimulate and the receptivity of "B" to stimulation with a corresponding increase in age. Cultures "A" and "B" twenty-five days old or older showed a reduced activity but nevertheless typical behavior in membrane-matings.

Filtrates and extracts of the culture medium but not the mycelium of "A" were shown to be active in stimulation of sex structures and lysis in "B" culture. Increase in assayable activity was correlated with the disappearance of carbohydrate and nitrogen from the culture medium. Ion exchange of active filtrates showed activity to be present only in the neutral fraction. The activity could be decreased by acidification and increased by alkalinization. Heating of the active filtrate to 40-45°C or above destroyed its capacity to stimulate.

Stimulation of sex structures was closely associated with mutual inhibition of growth as well as lysis and pathogenesis of the mycelium and developing sex structures of "B" under the above environmental conditions. By variation of the culture environment the incidence of this interculture pathogenesis and antagonism could be altered. Those conditions which allowed the most extensive association in dual culture, with the exception of addition of carbohydrates, stimulated an intense and widespread production of sex structures and a delayed but nevertheless severe pathogenesis and lysis. Under conditions allowing limited association and a stronger mutual inhibition of growth, sex structures were produced in limited numbers and severe pathogenesis and lysis of sex structures and mycelium of "B" were observed. Pathogenesis, lysis, and stimulation of sex structures in dual culture were nonexistent under conditions promoting a complete mutual inhibition of growth.

To ascribe a predominance to either organism in effecting stimulation would be inconsistent with the experimental results. Although the production of the stimulatory substance by "A" is essential for stimulation to take place, equally important is the capacity of "B" to resist penetration by inhibition of growth of the pathogenic culture. Penetration of the "B" culture by "A" is prerequisite to stimulation of sex structures. The action of the pathogenic culture subsequent to penetration could then be assumed to be a depression of the physiological activity of "B" which simultaneously disposed the culture to pathogenesis by the mycelium of "A" and induced the production of sex structures.

By culture filtrate experiments the stimulatory substance was shown to be elaborated in the absence of "B" culture. However, it seems a reasonable assumption, from comparison of the stimulation produced by filtrates and that produced by membrane matings, that the presence of "B" might be salutary to the production of the stimulatory substance by "A".

# COMPONENTS OF VARIANCE OF DIALLEL CROSSES OF MAIZE IN EXPERIMENTS REPEATED OVER LOCATIONS AND YEARS<sup>1</sup>

Dale Frederick Matzinger<sup>2</sup>

Department of Agronomy

In studies of the inheritance of quantitative characters it has not been possible to observe the effects of each gene individually as in the case of qualitative characters. The large number of gene pairs and the confusing effects of the environment mask the individual expression of each gene. Therefore, studies of the inheritance of these characters have been directed towards obtaining estimates of covariances between relatives in terms of the components of genotypic variance. From these estimates plant breeders are able to determine the most efficient types of breeding systems.

Various methods of obtaining theoretical covariance between relatives have been presented in the literature, each with a particular set of assumptions. The general case of random mating populations has been developed for an arbitrary number of alleles, arbitrary loci, and arbitrary epistacy. Most procedures which have been developed for inbred populations have assumed no epistacy.

In this study theoretical covariances between relatives were obtained for inbred populations in terms of a random mating population. Individuals in a random mating population are chosen at random, selfed, and used as parents to reconstruct a new population by making all possible intercrosses. The results apply to diploid populations for the general case of arbitrary alleles, arbitrary loci, arbitrary epistacy, and arbitrary inbreeding. The derivation was developed for a single locus with two alleles, extended to a single locus with arbitrary alleles, and finally extended to the case of two loci.

Covariances were expressed in terms of the components of genotypic variance, where the total genotypic variance for two loci is

$$\sigma^2_G = \sigma^2_A + \sigma^2_D + \sigma^2_{AA} + \sigma^2_{AD} + \sigma^2_{DD}$$

and

$$\sigma^2_G = \text{total genotypic variance}$$

$$\sigma^2_A = \text{additive genetic variance}$$

$$\sigma^2_D = \text{dominance variance}$$

<sup>1</sup>Doctoral thesis number 1790, submitted May 24, 1956. Chairmen of Committee, G.F. Sprague and I.J. Johnson, Department of Agronomy.

<sup>2</sup>B.S., Iowa State College, Ames. M.S., *ibid*.

Graduate Assistant, Agricultural Experiment Station.

$\sigma^2_{AA}$  = additive x additive epistatic variance

$\sigma^2_{AD}$  = additive x dominance epistatic variance

$\sigma^2_{DD}$  = dominance x dominance epistatic variance

The proportion of each of these components for the covariance of full-sibs was derived as

$$\begin{aligned} \text{Cov}(\text{FS}) = & \left(\frac{1+F}{2}\right) \sigma^2_A + \left(\frac{1+F}{2}\right)^2 \sigma^2_D + \left(\frac{1+F}{2}\right)^3 \sigma^2_{AA} \\ & + \left(\frac{1+F}{2}\right)^3 \sigma^2_{AD} + \left(\frac{1+F}{2}\right)^4 \sigma^2_{DD} \end{aligned}$$

and the covariance of half-sibs was

$$\text{Cov}(\text{HS}) = \left(\frac{1+F}{2}\right) \sigma^2_A + \left(\frac{1+F}{4}\right)^2 \sigma^2_{AA}$$

The extension to arbitrary loci was indicated.

The analysis of variance and expected mean squares were presented for the diallel cross for individual experiments and for experiments combined over locations and years in relation to the components of genotypic variance. Theoretical expectations of general and specific combining ability were obtained in terms of additive, dominance, and two-factor epistatic variances.

The variance of general combining ability contained a portion of the additive x additive epistatic variance in addition to additive genetic variance. The variance of specific combining ability contained dominance, additive x additive, additive x dominance, and dominance x dominance variances.

Under the assumption of no epistacy, estimates of additive and dominance variances were obtained from the diallel cross of ten  $S_1$  lines obtained at random by selfing in a random mating population in equilibrium. The experiment was repeated at three locations for a two-year period. There was a large fluctuation in the ratio of  $\sigma^2_D/\sigma^2_A$  between the six experiments indicating the limitation of these estimates when they are derived from an experiment grown at one location in a single year.

In the analysis combined over locations and years, the estimate of  $\sigma^2_A$  was almost negligible and the estimate of  $\sigma^2_D$  was relatively large. The estimate of the interaction component  $\sigma^2_{Ay}$  was very large relative to the other interaction components, a result of a shift in the effects of the genes from 1952 to 1953. This shift in expression of the genes accounted for the small estimate of  $\sigma^2_A$  in the combined analysis, since the additive genetic effects averaged to almost zero. This would have considerable relevance to breeding and testing procedures if it is substantially correct.

Before adequate interpretation can be given to studies on quantitative inheritance, information is needed on the importance of epistacy. A method is suggested which utilizes the variances which were derived to obtain estimates of epistatic components of genotypic variance.



SUBSTITUENT EFFECT IN 1,10-PHENANTHROLINE  
CHELATION KINETICS<sup>1</sup>Dale William Margerum<sup>2</sup>

Department of Chemistry

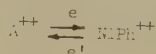
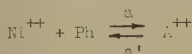
The nucleophilic character of the 1,10-phenanthroline type ligand was varied by the use of 5-methyl-1,10-phenanthroline, 1,10-phenanthroline and 5-nitro-1,10-phenanthroline. The degree to which these substituents affected the nucleophilic character was determined by the dissociation constants of their respective 1,10-phenanthrolium ions. The rates of reaction of each of these ligands were measured with nickel(II) and vanadium(IV) and compared with the rates of reaction with iron(II).

1. Nickel(II)

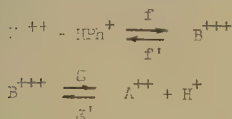
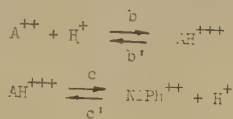
The rates of reaction of the mono-, bis-, and tris(1,10-phenanthroline) nickel(II) complexes are sluggish. The observed rate of formation constant,  $k_o$ , for the mono(1,10-phenanthroline)nickel(II) complex, based on first order nickel(II) ion concentration and first order free 1,10-phenanthroline concentration, is acid dependent. Ionic strength has little effect on the reaction rate. This acid dependence can be expressed mathematically as:

$$k_o = \frac{([H^+] + .0043)}{(.435[H^+] + .0431)} 10^6$$

An expression of this form can be derived by assuming the following reactions:



together with either one of the following two mechanisms:

1,10-phenanthrolium mechanismacid catalyzed mechanism

where Ph is 1,10-phenanthroline,  $Ni^{++}$  is  $Ni(H_2O)_6^{++}$ ,  $NiPh^{++}$  is  $Ni(H_2O)_4Ph^{++}$ ,  $B^{+++}$  is  $Ni(H_2O)_5HPh^{+++}$ ,  $A^{++}$  is  $Ni(H_2O)_5Ph^{++}$ , and  $AH^+$  is  $Ni(H_2O)_4(H_3O)Ph^{+++}$ . The complexes,  $A^{++}$ ,  $AH^{+++}$ , and  $B^{+++}$  are all considered to be unstable intermediates such as might result from only one bond formed between nickel(II) and 1,10-phenanthroline. Using appropriate approximations  $k_o$  can be expressed as:

$$k_o = \frac{[H^+] + m}{n[H^+] + p}, \quad \text{where } m, n, \text{ and } p \text{ are functions of}$$

<sup>1</sup>Doctoral thesis number 1711, submitted August 12, 1955.

Chairman of Committee, Chas. V. Banks, Department of Chemistry.

<sup>2</sup>B.A., Southwest Missouri State College, Springfield.

Junior Chemist, Institute for Atomic Research.

a, a', e, together with either f, f', g, g' or b, b', c.

The observed rate of dissociation constant,  $k'_0$ , for mono(1,10-phenanthroline)nickel(II) can be expressed similarly.

$$k'_0 = \frac{([H^+] + .015)}{(.14[H^+] + .060)} 10^{-3} = \frac{[H^+] + q}{r[H^+] + s},$$

where q, r, and s are functions of a', e, e' together with either f', g, g' or b, b', c, c'.

The 5-methyl-1,10-phenanthroline and 5-nitro-1,10-phenanthroline formation and dissociation rates have a similar acid dependence. The acid independent term,  $k_{if}$ , has the following values:

5-methyl-1,10-phenanthroline	$1.2 \times 10^5 \text{ min}^{-1}$
1,10-phenanthroline	$1.0 \times 10^5 \text{ min}^{-1}$
5-nitro-1,10-phenanthroline	$0.4 \times 10^5 \text{ min}^{-1}$

The values of the formation rate constants for the bis- and tris(1,10-phenanthroline)nickel(II) complexes are estimated to fall between  $10^4$  and  $10^5 \text{ min}^{-1}$ .

The following equilibrium constants were calculated from the spectrophotometric data:

mono(1,10-phenanthroline)nickel(II)	$K_1 = 2.5 \times 10^{-9}$
mono(5-methyl-1,10-phenanthroline)nickel(II)	$K_1 = 1.9 \times 10^{-9}$
mono(5-nitro-1,10-phenanthroline)nickel(II)	$K_1 = 2.7 \times 10^{-8}$
bis(1,10-phenanthroline)nickel(II)	$K_1 \approx 8.0 \times 10^{-9}$
tris(1,10-phenanthroline)nickel(II)	$K_3 = 2.8 \times 10^{-8}$

$$K_1 K_2 K_3 = K \approx 6 \times 10^{-25}$$

## 2. Iron(II)

The observed rate of formation constant for ferroin changes from  $1.3 \times 10^{19} \text{ min}^{-1}$  in 0.5 molar sulfuric acid to  $2.5 \times 10^{18} \text{ min}^{-1}$  in 0.01 molar perchloric acid. An acid dependent mechanism similar to that observed with nickel(II) is indicated. Although the observed rate of formation constant varies 160-fold with substituents, this appears to be largely due to changes in the equilibrium constants of the rapid forming mono- and bis- complexes. The actual rate of formation constant of tris(1,10-phenanthroline)iron(II) from bis(1,10-phenanthroline)iron(II) seems insensitive to changes in the nucleophilic character of the 1,10-phenanthroline nitrogens.

## 3. Vanadium(IV)

The mono(1,10-phenanthroline)vanadium(IV) complex is the predominant species found in 0.01 molar acid solutions. The rates of formation constants for the mono- complexes of 1,10-phenanthroline, 5-methyl-1,10-phenanthroline and 5-nitro-1,10-phenanthroline with vanadium(IV) are  $3.1 \times 10^4 \text{ min}^{-1}$ ,  $3.9 \times 10^4 \text{ min}^{-1}$ ,  $1.6 \times 10^3 \text{ min}^{-1}$ , in 0.3 molar perchloric acid.

A comparison of the nickel(II)-, iron(II)-, and vanadium(IV)-1,10-phenanthroline systems shows that the rate constant for the rate determining step is in order of decreasing value for iron(II), nickel(II) and vanadium(IV). The substituent effect on this same rate constant appears to be in the reverse order, with vanadium(IV) showing the largest substituent effect.

An analytical separation of iron(II) from vanadium(IV) and nickel(II) is made by taking advantage of the different rates of reaction of these ions with 1,10-phenanthroline. It is possible to improve upon this separation by utilizing the substituent effect on the equilibria and rates of reaction of the various species involved. Thus, 5-methyl-1,10-phenanthroline at a high pH and 5-nitro-1,10-phenanthroline at a low pH serve as better chelates than 1,10-phenanthroline, itself in carrying out this separation.

The ability to vary the relative rates of formation of metal chelates by changes in the nucleophilic character of the ligands and in the acidity of the solution should make possible many additional analytical separations of metal ions.

# OPTIMUM FEED COMBINATIONS AND MARKET WEIGHTS FOR BROILERS BASED ON TWO-VARIABLE PRODUCTION FUNCTIONS<sup>1</sup>

Robert Hubert McAlexander<sup>2</sup>

Department of Economics and Sociology

The main objectives of this study were to use experimental data as a basis for prediction of, a) least-cost rations for broilers for various prices of soybean oil meal and corn, b) the most profitable marketing weights for broilers on different protein rations with various broiler and feed prices, and c) least-time protein rations for broilers. In order to attain these objectives, it was necessary to estimate input-output relationships for various combinations and amounts of corn and soybean oil meal and broiler gains. From these basic relationships it was possible to estimate isoquants, marginal rates of substitution of soybean oil meal for corn, and marginal productivities of feeds.

Data for this study were obtained from an experiment conducted in the winter and spring of 1955. Rations of 16, 18, 20, 22, 24, and 26 per cent protein were fed to 600 New Hampshire chicks. The 600 chicks were randomly assigned to 30 batteries with 10 cockerels and 10 pullets per battery. During the feeding period, 12 batteries of birds received the same protein rations (two batteries on each ration); 18 batteries were fed to an average weight of 1.32 pounds on various rations, then each battery was changed to a lower protein for the remainder of the feeding period.

Several types of mathematical functions shown below were used for predicting input-output relationships based on the experimental data. Quadratic function (7) was selected as a basis for predicting the most profitable marketing weights; logarithmic function (9) was selected as a basis for predicting the "average" least-cost ration fed for the complete production period; logarithmic interval functions (28) and (29) were used as a basis for predicting "average" least-cost rations for feeding two different rations during the production period.

$$(7) Y = 0.0331 + 0.4823C + 0.6415S - 0.01828C^2 - 0.04973S^2 - 0.02321CS$$

$$(9) Y = 0.9922C^{0.5537} S^{0.3371}$$

$$(28) Y = 1.0754C^{0.5425} S^{0.3837} \quad (\text{up to a weight of 1.32 lbs.})$$

$$(29) Y = 0.7021C^{0.6463} S^{0.2944} \quad (\text{weight above 1.32 lbs.})$$

Least-cost "average" rations were estimated for a wide range of corn and soybean oil meal prices by, a) determining contour equations for the logarithmic functions, b) finding derivatives of these functions with respect to

<sup>1</sup>Doctoral thesis number 1758, submitted January 16, 1956. Chairman of Committee, E. O. Heady, Department of Economics and Sociology.

<sup>2</sup>B.S., Iowa State College, Ames. M.S., Oregon State College, Corvallis. Associate, Agricultural Experiment Station.

soybean oil meal, and c) equating marginal rates of substitution,  $\frac{dC}{dS}$ , with the soybean oil meal to corn price ratios. Least-cost "average" rations using various feed costs are presented in tables and also summarized in the form of a "graphic guide."

The most profitable marketing weights above feed costs were determined for a wide range of feed-broiler price ratios for broilers fed protein rations varying from 15 to 27 per cent by 0.5 per cent intervals. These optimum broiler weights were determined by, a) expressing corn and soybean oil meal inputs from quadratic over-all function (7) in terms of feed inputs representing protein rations of specific percentages, b) finding derivatives of these functions with respect to feed and equating with feed-broiler price ratios. c) substituting optimum feed quantities found in (b) above into the gain-feed function for each of the protein rations, and d) adding the initial average weight of chicks to the optimum gains. Optimum weights are presented in tables in the text and also in the form of "graphical guides" which provide an approximation of optimum marketing weights, feed consumption and time requirements for broilers on the various protein rations.

The polynomial square root function (41) below was used to predict time required for feed inputs and in turn, time requirements for optimum weights and other specific weights.

$$(41) T = 0.6735 + 4.7974C + 9.4576S + 21.4617C + 13.6188S - 12.0286CS$$

For broilers marketed at approximately 3.25 pounds liveweight, a protein ration between 21 and 21.5 per cent over the entire production period provides the most rapid gains. When the total production period is broken into two intervals, a slightly higher protein ration provides the most rapid gains at lighter weights; a slightly lower protein ration provides the most rapid gains at heavier weights. Under the average soybean oil meal and corn prices for 1950-1954, the "average" least-cost rations for broilers do not coincide with the least-time rations. Least-cost rations consist of, a) an 18.5 per cent ration for the entire period, b) a 19 per cent ration for the first weight interval, and c) a 16.5 per cent ration for the second portion of the feeding period. Thus, poultrymen must compare least-cost and least-time rations for determining the most profitable rations for broilers.

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ECONOMICS OF CORN-SOYBEAN OIL MEAL SUBSTITUTION  
FOR HOGS ON PASTURE<sup>1</sup>Dean Elgar McKee<sup>2</sup>

Department of Economics and Sociology

The objectives of this study were to estimate for hogs fed on alfalfa pasture:

1. The relationship between the inputs of corn and soybean oil meal and body weight gains.
2. The rate of substitution between corn and soybean oil meal when fed in different proportions and at different levels of output.
3. The corn-soybean oil meal feed combination which will produce hog gains at minimum cost at various ratios of the price of soybean oil meal to the price of corn.
4. The relationship between corn and soybean oil meal inputs and the rate of body weight gains.
5. The difference in returns over feed costs between the least-cost and least-time feeding systems on the basis of past feed and hog prices.
6. The effect of pasture on the feed-gain relationships by comparing the relations obtained in the pasture study to the relations obtained in an earlier drylot study.

Two experiments were conducted cooperatively by the Departments of Animal Husbandry and Economics and Sociology to obtain the necessary data to estimate the desired feed-gain relations under a pasture feeding system. Six rations were fed in the experiments. They were 8 per cent, 10 per cent, 12 per cent, 14 per cent, 16 per cent, and 18 per cent protein. The hogs were individually fed in portable pasture units and each hog received the same ration throughout the course of the experiment. The two experiments included a total of 72 hogs.

Several types of equations were examined as possible alternatives for expressing the relationship between corn and soybean oil meal inputs and body weight gains. The functions examined were the Cobb-Douglas, a quadratic, and a quadratic square root. The procedure of dividing the production period into intervals on the basis of weight and fitting a separate Cobb-Douglas function to each interval was examined as another possible alternative. The economic analysis of corn-soybean oil meal substitution was carried through on the basis of the feed-gain relationship as expressed by the quadratic function.

A given level of gain can be produced by many different combinations of corn and soybean oil meal quantities. The one combination which will produce the desired gain at minimum feed costs is attained when the feed proportions in the ration are adjusted so the rate of substitution between the feeds is equal to the ratio of the feed prices. Variation in the feed price ratio will necessitate variation of the feed proportions if feed costs are to be minimized.

If the proportions in which the feeds are consumed are to be kept under control it is necessary to grind and mix the ration. The cost of grinding and mixing can be eliminated by following a free-choice feeding system; however, if the feeds are consumed under a free-choice system in proportions which differ considerably from the minimum cost proportions, the feed cost under the free-choice system may exceed the feed cost plus grinding and mixing

<sup>1</sup>Doctoral thesis number 1740, submitted December 6, 1955. Chairman of Committee, Earl O. Heady, Department of Economics and Sociology.

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costs under the controlled system. The range of feed proportions within which the free-choice system will be more economic than the minimum feed cost system will vary with variations in the cost of the feeds relative to the cost of grinding and mixing. When the feed cost is relatively high the range of feed proportions is more narrow than when the feed cost is relatively low, cost of grinding and mixing being constant.

Returns over feed costs are shown to be greater under the least-cost system of rations a greater proportion of the time than if the hogs were fed to maximize the rate of gain. The advantage of the least-cost system is greatest at early farrowing dates. Rate of gain becomes more critical at farrowing dates later in the season because of the seasonal decline in hog prices.

The results of the study did not show the pasture feeding system to have any advantage over a drylot system in terms of feed efficiency. As much corn and soybean oil meal was required on pasture to produce a hundred pounds of gain as was required on drylot. Those differences that did appear in the feed requirements under the two systems were not statistically significant. The rates of substitution did differ significantly between pasture and drylot feeding. With a given corn-soybean oil meal price ratio, the least-cost ration on drylot would have a lower protein content than the least-cost ration for pasture.

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#### DEVELOPMENT AND USE OF VISUAL MATERIALS FOR TRAINING FOOD SERVICE EMPLOYEES IN WORK SIMPLIFICATION<sup>1</sup>

Marjorie Marie McKinley<sup>2</sup>

Departments of Institution Management and of Home Economics Education

The purposes of the research were: 1. To select appropriate available visual materials and to develop additional visual materials for training food service employees in work simplification. 2. To plan and try out work simplification training for a group of food service employees using the visual materials selected and developed. 3. To secure information relative to the outcomes of the training program in order to formulate hypotheses regarding the training of employees and specifically in regard to the use of visual materials for teaching work simplification. 4. To provide a basis for recommending methods of research for similar studies.

The first step was to define the objectives of work simplification training for employees: 1. To provide an understanding of work simplification which will make the workers receptive to analysis of their jobs, to methods proposed by management, and to adoption and use of the methods prescribed. 2. To improve management-labor relations and increase the interest of employees in their work. 3. To stimulate employees to make suggestions for improving work methods. 4. To assist the workers to improve these methods of work which are determined by them. 5. To lower costs. 6. To give impetus to a continuing program of work simplification. With recognition of these objectives the work simplification generalizations, on which the training program was based, were formulated.

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<sup>1</sup>Doctoral thesis number 1813, submitted June 5, 1956. Chairmen of Committee, Grace M. Augustine, Department of Institution Management, and Hester Chadderdon, Department of Home Economics Education.

<sup>2</sup>B.S., Indiana University, Bloomington. M.A., Columbia University, New York City. Assistant Professor.

Five motion pictures and a small booklet, which related work simplification to homemakers' tasks, were selected for use in the training program. The visual materials developed included 67 colored slides and an illustrated booklet.

As a basis for determining the workers' understanding of work simplification, situation tests were developed to be administered to the employees before and after the training program. In these tests, work situations were presented by means of motion pictures, and each employee was asked to make suggestions orally for simplifying the methods used.

The work simplification training was conducted in the food service unit of the men's residence hall on the Iowa State College campus. At individual interviews with each full-time employee the pretest was administered and certain personal data were collected. The posttest was administered in individual interviews four weeks after the conclusion of the training classes. At these latter interviews the employees were asked to evaluate the work simplification program. The pretest was administered as a retest approximately six months after it was first given.

Following the pretest, for three and one-half weeks, many of the work processes used by the employees were observed and recorded in order to select appropriate illustrations for use in the training classes. Other purposes of these observations and subsequent analyses and improvements were to provide on-the-job examples of how a process could be improved by the application of work simplification generalizations and to determine the employees' reactions to having their work methods studied, the extent to which the employees would make suggestions for improving work methods, and whether they would adopt and use new work methods later proposed.

Seven work simplification classes were conducted; the visual materials previously selected and developed were used in these classes. Following these classes, during a period of five weeks, there was further study of work methods in the kitchen and dining room. Improved methods were developed and installed for several work processes.

There was a variety of outcomes resulting from the training program. Progress was made in improving work methods. Employees who participated in or had direct contact with work process studies gave excellent cooperation when work methods were being analyzed and improved methods developed. Employees who were asked to adopt new work methods did so. It is not known to what extent the excellent cooperation of the workers was the direct result of the training classes and the procedures used during the training program. Employees made suggestions for improving work methods both in the classes and during the work process studies. The workers evidenced an understanding of the viewpoint of management. Of the 23 workers, 18 indicated that the work simplification classes had been beneficial for them. The situation tests developed for evaluating the employees' understanding of work simplification were not entirely satisfactory as instruments of evaluation; however, analyses made of the test scores gave some indication that the employees' ability to apply work simplification generalizations was greater following the training program.

On the basis of the experiences in this research recommendations were made regarding research methodology for similar investigations. Generalizations related to training food service employees and specifically to the use of visual materials for training food service employees in work simplification were formulated. Those which, on the basis of the present research and the experiences and recommendations reported in the literature, appear to be generally accepted were stated as assumptions. The following fifteen generalizations were formulated as hypotheses; when reference is made to work simplification training for employees, it is assumed that the objectives for training correspond to those of this study.

Hypotheses:

1. If such visual materials as appropriate motion pictures and colored slides are available for training employees, their use is more economical of the trainer's time and is as effective as actual demonstration to teach work simplification.
  2. Proper use of appropriate visual materials in work simplification classes for employees facilitates communication between the trainer and employees, decreases time necessary for training, and helps to gain and hold the interest of employees in the training program.
  3. Use of visual materials to depict work situations before and after improvement of work methods promotes interest in a work simplification program.
  4. Visual materials are most effective for training employees if they illustrate the application of work simplification generalizations in the types of work which are performed in a food service operation.
  5. Work simplification training is effective for workers with low morale as well as for workers with high morale.
  6. A work simplification training program for employees contributes to harmonious management-labor relations.
  7. Provision in a training program of an understanding of work simplification by food service employees contributes to harmonious management-labor relations because it provides workers with additional understanding of management problems and a means whereby employees may contribute to management decisions which affect the employees' work.
  8. By work simplification training employees become more receptive to analysis of their jobs, to work methods proposed by management, and to adoption and use of methods prescribed.
  9. By acquiring an understanding of work simplification in a training program, employees become more receptive to analysis of their jobs, to work methods proposed by management, and to adoption and use of methods prescribed.
  10. Work simplification training classes for employees are most effective if the classes are spaced over a reasonable period of time rather than concentrated with a very short period. Follow-up or refresher classes after the original training classes reinforce the learning.
  11. Work simplification classes for employees are more effective if supplemented by the employees' participation in or contact with actual simplification of work methods on the job.
  12. Improved methods adopted by employees as the result of a work simplification training program will continue to be used until a better method is developed.
  13. Many employees who participate in work simplification training make some usable suggestions for improving work methods and will improve methods of work determined by them.
  14. Suggestions made by employees in regard to simplifying work methods are most often related to changes in equipment or other physical facilities. Work simplification training provides a basis for employees to evaluate the practicality of such suggestions from the standpoint of effect on other work procedures and economic feasibility.
  15. Suggestions which a worker makes for simplifying methods used in a specific work situation are associated to some extent with work procedures in which he has participated or which he has observed.
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THE INFERENCE OF ADSORPTION FROM  
DOUBLE LAYER CAPACITY STUDIES<sup>1</sup>Robert Edward Minturn<sup>2</sup>

Department of Chemistry

The effect of surface active components on the electrical double layer capacity at the mercury--0.10 N aqueous perchloric acid solution interface was investigated. Concentration of the surface active components were varied from zero to saturation and the mercury electrode polarizing potentials were varied from 0.5 volt cathodic to 0.5 volt anodic with respect to the electrocapillary maximum. Surface active components investigated were pentanoic acid, 1-pentanol, 3-pentanone, pentanenitrile, and octanoic acid.

A theory permitting the interpretation of apparent surface coverage by adsorbed surface active components in terms of actual surface coverage was developed, reduced to a form suitable for the treatment of data in the special case of the "regular" monolayer, and the resulting equations applied to the experimental data.

The theoretical treatment predicts, and the experimental results confirm, a strong dependence of apparent surface coverage upon polarizing potential at fixed adsorbate activity. The curve has a maximum in the neighborhood of, but not in general at, the potential of the electrocapillary maximum. To either side of the maximum, the apparent coverage decreases sharply, undergoes a change in sign, and passes through pronounced minima. At high polarizing potentials, both cathodic and anodic, the apparent coverage approaches zero. Curves calculated from the theoretical treatment represent the data almost quantitatively in the neighborhood of the maximum and semiquantitatively in the regions of pronounced curvature.

The theoretical treatment contains the molar area as an adjustable parameter, so that in principle not only fractional surface coverages but also actual amounts adsorbed can be calculated from the dependence of the apparent coverage on polarizing potential.

Calculated molar areas are somewhat larger than one would expect from close-packed models and vertical orientation. Areas for 3-pentanone and pentanenitrile indicate the possibility of orientation parallel to the surface, and the areas indicated for pentanoic acid and octanoic acid suggest the possibility that these molecules are hydrated on the surface.

Standard free energies of adsorption are computed, referred to solute saturated with water as solution standard state and complete coverage as the surface standard state. Pentanoic acid, 1-pentanol, and octanoic acid were found to have substantially the same free energies of adsorption ( $2.62 \pm 0.8$  Kcal/mole); the standard free energy of adsorption of pentanenitrile was somewhat less, about 2.44 Kcal/mole, and that of 3-pentanone was markedly higher (3.15 Kcal/mole).

Apparent surface coverages coincide with actual surface coverages only in the neighborhood of the maximum of the apparent coverage--polarizing potential curve. For reliable inference of adsorption from double layer capacity it is therefore essential that a sufficient range of polarizations be investigated to establish the location of this maximum.

<sup>1</sup>Doctoral thesis number 1737, submitted December 2, 1955.

Chairman of Committee, Robert S. Hansen, Department of Chemistry.

<sup>2</sup>B.S., Oregon State College, Corvallis.

Research Associate, Institute for Atomic Research.

ORGANIC PHOSPHATE INSECTICIDES AS SEED TREATMENTS  
ON CORN, SOYBEANS AND SORGHUM<sup>1</sup>Wallace Clark Mitchell<sup>2</sup>

Department of Zoology and Entomology

Germinator, greenhouse, and field tests were carried out in 1954 and 1955 to evaluate the direct effects of four organic phosphate and two chlorinated hydrocarbon insecticides as seed treatments on corn, soybeans, and sorghum. An exploratory laboratory test was made to determine the effectiveness of these insecticide treatments in protecting seed corn from wireworm damage. Correlations between certain field and laboratory data were computed to see how closely the two kinds of measurements were related.

Four organic phosphate (chlorthion, Diazinon, EPN, and malathion) and two chlorinated hydrocarbon (dieldrin and lindane) insecticides were applied at rates of 0.5, 1, and 2 ounces, respectively, per bushel of seed, all in wettable powder formulations. A fungicide, Arasan SF-X, and a sticker, methyl cellulose, were applied to all treatments except an untreated control. All of the seed was treated in quart fruit jars. The jars were shaken by hand and rotated on an electric laboratory mixer to distribute the chemicals uniformly over the seed. All treated seed was stored at room temperature in the containers in which it had been treated. Germinator and greenhouse tests were carried out 6 days, 9 months, and 13 months, respectively, after treatment. Hand-planted field experiments were carried out both in 1954 and 1955.

Pioneer 349 hybrid corn, Hawkeye soybeans, and Atlas sorghum were the varieties used in all experiments.

The principal criteria used for measuring treatment effects on seeds and seedlings in the laboratory tests were radicle and plumule lengths, seedling green weights, total germination, and mean emergence period. The rolled towel or "paper doll" technique was used in the germinator tests. Washed river sand in metal greenhouse flats was used in all the greenhouse experiments. Stand, yield, and mean emergence period data were used to evaluate the seed treatments in the hand-planted field experiments.

Chlorthion was the most phytotoxic material used in these tests. The 1 and 2 ounce dosages significantly reduced stands of all three crops when the seed had been stored for 9 months. When seed with the 2 ounce level was tested at the end of 13 months in storage none of the corn germinated, and only about 3 per cent of the sorghum and 10 per cent of the soybeans germinated in laboratory tests. The 1955 field tests with the same dosage of chlorthion gave 15 and 25 per cent stands for sorghum and soybeans, respectively, while none of the corn germinated. Adverse results were also evident when green weights and radicle lengths of seedlings were measured.

Malathion was phytotoxic but less so than chlorthion. Slight injury appeared after 9 months in storage with the 1 and 2 ounce dosages. Increasing the storage period to 13 months accentuated these effects, although the 2 ounce level did not completely inhibit corn germination. Corn was most sensitive to malathion seed treatments, with sorghum and soybeans following in this order.

Diazinon did not appear to be phytotoxic at the 0.5 and 1 ounce dosages in these experiments. However, seed treated with the 2 ounce level and stored for 13 months showed significant reductions in stand. This insecticide was less toxic to corn than either chlorthion or malathion, and soybeans and sorghum appeared to be even less susceptible to Diazinon injury than corn.

<sup>1</sup>Doctoral thesis number 1707, submitted August 9, 1955.

Chairman of Committee, J.H. Lilly, Department of Zoology and Entomology.

<sup>2</sup>B.S., Iowa State College, Ames. M.S., *ibid*.

Graduate Assistant, Division of Science



EPN appeared to be the least phytotoxic of the four phosphate insecticides tested. However, the highest dosage (2 ounces per bushel of seed) caused statistically significant reductions in stand after 13 months in storage. These stand reductions were not as great as those from Diazinon, malathion and chlorthion.

Lindane seed treatment was phytotoxic to all three crops in tests conducted shortly after the seed had been treated. The radicle lengths of the seedlings were significantly shorter than the other treatments when the treated seed had been stored for 6 days. These toxic effects were less evident when the seed was planted in the field, and they decreased as the storage period was increased. Corn and sorghum were more sensitive than soybeans to lindane seed treatment.

Dieldrin appeared to be the best seed treatment insecticide investigated. It gave favorable stand counts, green weights, and radicle and plumule lengths for all three crops. Even after the treated seed had been stored for 13 months at room temperature most of the results with dieldrin-treated seed compared favorably with the control results.

The phytotoxic effects of the insecticides increased with the rates of application for all insecticides that showed adverse effects. The phytotoxic effects appeared to increase as the storage period increased for all materials except lindane.

In laboratory tests with the wireworm, *Melanotus communis* Gull., Diazinon, EPN, lindane, and dieldrin gave the highest wireworm mortalities. However, an analysis of the data failed to reveal any significant differences between the treatments.

Correlations were computed between certain field and laboratory data in an attempt to determine which laboratory measurements best indicate the treatment effects that may occur in the field. Significant correlations were obtained between corn yield data from a hand-planted field experiment and average green weights of seedlings in germinator ( $r = 0.972112$ ) and greenhouse ( $r = 0.995903$ ) tests. A correlation between the mean emergence period of corn in a field experiment and a greenhouse experiment also revealed a significant correlation coefficient ( $r = 0.965697$ ) between the two.

Correlations between field stands and total germinations in the laboratory were computed for all three crops. Significant correlation coefficients were obtained between field stands and total germinations in the germinator for corn ( $r = 0.987125$ ), soybeans ( $r = 0.977619$ ), and sorghum ( $r = 0.551801$ ). The correlation coefficients between field stands and greenhouse germinations were significant for corn ( $r = 0.985770$ ), soybeans ( $r = 0.923025$ ), and sorghum ( $r = 0.640265$ ). All the data in these correlations were from field and laboratory experiments carried out after comparable periods of storage.

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CORRELATIONS OF SOIL AND PLANT MEASUREMENTS  
OF PHOSPHORUS AVAILABILITY<sup>1</sup>Ursula Siegrist Moser<sup>2</sup>

Department of Agronomy

The main objective of the research described herein was to evaluate the Amer anion exchange resin method for estimating soil phosphorus availability by comparing it with other methods in current use. The basis of comparison was the correlation coefficients between the yield of phosphorus in plants grown on a group of soils and the results of laboratory measurements made by the various methods on the same soils.

Since most methods will give results that correlate well with plant response if the range in the properties of the soils is restricted sufficiently, a group of 22 soils with widely divergent properties was selected from different regions of the United States as a means of providing a rigorous test of the methods. The soils were selected from those used in the 1951 and 1952 cooperative uniform phosphorus experiments carried out nationally. The soils were selected to produce a poor correlation between Fried and Dean  $A$  values and soil phosphorus extracted by methods IA of Bray and Kurtz.

The experimental technique utilized in the greenhouse was designed to make phosphorus the limiting factor by adding ample quantities of nutrients other than phosphorus, and restricting the quantity of soil to 400 grams in a mixture with 3600 grams of quartz sand. Sorghum (variety Red Bine 60) was used as a test plant. The plants were allowed to grow until all were strongly deficient in phosphorus. The plants were then harvested and analyzed for phosphorus.

Four extraction procedures were used: (1) the buffered 0.5  $M$  sodium bicarbonate extraction method of Olsen *et al.*, (2) the 0.1  $N$  hydrochloric acid and the 0.03  $N$  ammonium fluoride extracting procedure of Bray and Kurtz, (3) the 0.01  $M$  calcium chloride extracting method of Schofield, as described by Aslyng, and (4) the anion-exchange resin method of Amer. Each method was employed with soil samples that were dry initially, and with soil samples that had been adjusted to moisture equivalent, and allowed to incubate at room temperature for a period of 7 days.

The method suggested by Aslyng involves the use of two different weights of soil in a fixed volume of 0.01  $M$  calcium chloride solution. The molar phosphate concentration in solution with the different quantities of soil was plotted against the reciprocal of the weight of soil to obtain a straight line that was extended to the Y axis. The intersection of this line with the Y axis gave the molar phosphate concentration at "zero dilution." From this value, together with knowledge of the pH and the calcium activity in the calcium chloride solution, the phosphate potential ( $\frac{1}{2}pCa + pH_2PO_4$ ) was calculated.

Schofield stated that perhaps it is not the amount of available phosphate in a soil that primarily controls the uptake of phosphorus by plants, but the work needed to withdraw it from the soil. Hence he conceived of the phosphate potential or free-energy concept of plant utilization of soil phosphorus. Aslyng has stated that this potential should give a good estimate of soil phosphorus available to plants. The correlations between the phosphate potential and the yield of phosphorus indicated, however, that essentially no relationship existed between the two sets of data; the correlations were  $r = 0.07$  and  $r = -0.08$  for the dry and premoistened samples, respectively. Therefore, it may

<sup>1</sup>Doctoral thesis number 1789, submitted May 21, 1956.

Chairman of Committee, C.A. Black, Department of Agronomy.

<sup>2</sup>B.A., Hunter College, New York City. M.S., Kansas State College, Manhattan. Graduate Assistant, Agricultural Experiment Station.

be concluded that this method was not able to withstand the rigorous test presented by using soils that have widely divergent properties. The linear correlations ( $r$ ) obtained between phosphorus extracted for 20- and 40-gram weights of soil and the yield of phosphorus in milligrams were 0.61 and 0.63, respectively, for the dry treatment and 0.64 and 0.59 for the premoistened treatment. The correlations obtained between phosphorus extracted at zero dilution and the yield of phosphorus were 0.30 and 0.41 for the dry and premoistened treatments, respectively.

The correlations between yield of phosphorus and soil phosphorus extracted by the Bray and Kurtz method were low; the correlation coefficients were  $r = 0.38$  and  $r = 0.14$  for initially dry and premoistened samples, respectively. The unduly large amount of phosphorus extracted from some of the alkaline soils appeared to be primarily responsible for the low correlations.

Correlations between yield of phosphorus in the plants and soil phosphorus extracted by the 0.5 M sodium bicarbonate method of Olsen *et al.*, were higher than those described above, and were essentially the same with both the dry samples and the premoistened samples ( $r = 0.74$ ,  $r = 0.77$ , respectively).

The method of Amer involved extracting phosphorus from soils by a strong-base type anion-exchange resin (Dowex 2) employed in chloride form. The simple correlations between yield of phosphorus in the plants and phosphorus extracted from the soils over different lengths of time ranging from 5 minutes to 72 hours were about  $r = 0.78$  and  $r = 0.79$  with the dry and premoistened samples, respectively.

Two more complex types of correlations were investigated with the Amer method. In the first of these the phosphorus adsorbed from the soil by the resin was classified into different categories according to the time interval during which adsorption occurred. The intervals employed were 0 to 0.25 hour, 0.25 to 2 hours, 2 to 24 hours, and 24 to 72 hours. The phosphorus extracted during various time intervals was correlated with the yield of phosphorus in the plants by the method of multiple linear correlation. The multiple correlation coefficient ( $R$ ) obtained by arranging the data in this fashion were 0.86 and 0.87, for the dry and premoistened samples, respectively. These values are higher than the simple correlations described above.

The second multiple correlation analysis was made on the basis of quantities of soil phosphorus found in a different way. The over-all phosphorus extraction-time curve was broken down into component curves on the assumption that the process of phosphorus adsorption by the resin under the conditions found in the soil is first-order with respect to phosphorus. From one to four separate first-order reactions for each soil were found in this way, each reaction being characterized by a rate and by a maximum or limiting value that is approached as the time increases indefinitely. The limiting values were classified into four categories according to rate, and a multiple linear correlation was made between the limiting values as independent variables and the yield of phosphorus in the plants as the dependent variable. The multiple correlation coefficient was found to be  $R = 0.79$  where the independent variables were derived from analyses on samples of dry soil and  $R = 0.90$  where the independent variables were derived from the samples of premoistened soil. Although the former is no higher than the simple correlation coefficients obtained with the phosphorus extracted during a fixed length of time, the latter is the highest of all the correlation coefficients encountered in this investigation.

The results show that the yield of phosphorus in plants grown on a group of widely different soils was predicted more precisely by the Amer anion-exchange resin method for estimating soil phosphorus availability than by any of the other methods investigated. Predictions from measurements made by the Amer method appear to be somewhat improved by the use of premoistened soil samples instead of dry samples, and by breaking down the over-all phosphorus extraction versus time curve into a series of separate first order reactions.

HEATS OF DILUTION AND RELATED THERMODYNAMIC  
PROPERTIES OF AQUEOUS NEODYMIUM CHLORIDE  
AND ERBIUM CHLORIDE SOLUTIONS<sup>1</sup>

Alfred Wayne Naumann<sup>2</sup>

Department of Chemistry

A differential calorimeter has been constructed to measure the heats of dilution of electrolytic solutions. The differential method made possible the determination of heats of dilution to within a few thousandths of a calorie. Precision of this order was necessary to obtain meaningful values for the thermodynamic properties of very dilute solutions.

The heats of dilution of neodymium chloride and erbium chloride solutions have been measured at 25°C for concentrations up to 0.2 molal. Empirical expressions for the relative apparent molal heat content of the solute,  $\Phi_L$ ; the relative partial molal heat content of the solvent,  $\bar{L}_1$ ; and the relative partial molal heat content of the solute,  $\bar{L}_2$ , have been derived from the heats of dilution. The following equations have been derived for neodymium chloride solutions:

$$\Phi_L = 6925 m^{1/2} - 16725 m + 22278 m^{3/2} - 7596 m^2,$$

$$\bar{L}_1 = -62.37 m^{3/2} + 301.32 m^2 - 602.04 m^{5/2} + 273.70 m^3,$$

$$\bar{L}_2 = 10387 m^{1/2} - 33450 m + 55695 m^{3/2} - 22788 m^2.$$

The corresponding equations for erbium chloride solutions were as follows:

$$\Phi_L = 5687 m^{1/2} - 8637 m + 7066 m^{3/2},$$

$$\bar{L}_1 = -51.23 m^{3/2} + 155.60 m^2 - 190.95 m^{5/2},$$

$$\bar{L}_2 = 8531 m^{1/2} - 17274 m + 17665 m^{3/2}.$$

The thermodynamic properties of neodymium chloride and erbium chloride solutions were the same, within experimental error, for concentrations above 0.02 molal. For concentrations below  $4 \times 10^{-4}$  molal, the thermodynamic properties of neodymium chloride solutions followed the Debye-Hückel law predictions, but the thermodynamic properties of erbium chloride solutions appeared to depart from theoretical predictions.

<sup>1</sup>Doctoral thesis number 1794, submitted May 25, 1956.

Chairman of Committee, Frank H. Spedding, Department of Chemistry.

<sup>2</sup>B.A., Grinnell College, Grinnell, Iowa.

Research Assistant, Institute for Atomic Research.

PASSAGE OF FREE ELECTRONS THROUGH CERAMIC MATERIALS<sup>1</sup>Roger Emerson Nolte<sup>2</sup>

Department of Electrical Engineering

Ceramic discs, if sufficiently porous, are permeable to free electrons under the influence of an electric field. Plate characteristics, taken from tests on a diode circuit, exhibit curves that consist of three important parts: cutoff or the voltage at which plate current is just measurable, the concave upward or space-charge-limited part, and the concave downward portion where temperature saturation is apparent. The controlling factor in the first two cases is the space-charge that exists near the cathode side of the porous disc. At high plate voltages the saturation becomes complete as all the emitted electrons are transferred directly to the plate; which means the limiting electron cloud is dissolved.

More specifically the conditions at cutoff are caused by the electron cloud which creates a negative potential sheath,  $V_m$ , at the cathode side of the disc. By using the triode analogy, the effectiveness of the plate voltage is reduced by the constant  $w$  so that the plate current is given by

$$I = K(V_m + V_p/w)^a. \quad (11)$$

Here,  $V_m$  is not independent of  $V_p$  and increases from negative to positive values as  $V_p$  increases. Cutoff occurs when the negative  $V_m$  is equal in magnitude to  $V_p/w$ .

As  $V_p$  rises above the cutoff value the plate current rises as an exponential function of  $V_p$ . The exponent in this case is greater than that predicted by the Child-Langmuir space-charge equations of an ordinary vacuum tube. The highly random pore shapes which offer transmission paths having a variety of areas ( $A_k$ ) and lengths ( $l_k$ ) defy accurate quantitative derivations. A qualitative treatment uses  $n$  parallel transmission paths where the total current is given by

$$i_t = 2.33 \times 10^{-6} h \sum_{k=1}^n \frac{A_k V_p^{a_k}}{l_k^2} \quad (10)$$

where  $h$  is the electron velocity reduction factor caused by inelastic collisions. In this equation  $A_k$  and  $l_k$  are nearly constant for a given sample but the areas,  $A_k$ , are highly variable. As the plate voltage  $V_p$  increases, the larger areas conduct first. Such conduction decreases the density of the blocking electron sheath and conduction spreads to smaller areas in a cumulative action. This increasing area and the changing  $V_m$ , both being a function of  $V_p$ , result in the space-charge-limiting diode equation

$$i = K V_p^a. \quad (13)$$

The value of " $a$ " is obtained as the slope of the log-log plot of  $i$  vs  $V_p$ , and was found to vary from 2.4 to 15.2 for the samples tested.

When the electrons are given initial velocities by making the grid of a triode device positive, the cutoff potential is reduced. The electrons divide between the grid and the plate. At low plate voltages, the electrons that enter

<sup>1</sup>Doctoral thesis number 1689, submitted June 24, 1955. Chairman of Committee, W. L. Cassell, Department of Electrical Engineering.

<sup>2</sup>B.S., Iowa State College, Ames. M.S., *ibid*.

Graduate Assistant, Engineering Experiment Station.



the restricted ceramic-filled region between the grid and the plate lose their initial energies and establish the blocking sheath of electrons. The shape of the triode plate characteristics are similar to those of the corresponding diodes except for the reduced cutoff voltages.

Some of the factors affecting the transmission of electrons through porous ceramic discs are: the length of the electron path, the number and size of the transmitting areas, and the density of the closed pores or electron traps. The density by weight of the porous ceramic is not an effective measure of its permeability to electron flow. More important is the density of open pores that do not trap or block the electron's progress to the attracting electrode.

For purposes of application, the porosity of the ceramic material need not come from the loose packing or from the firing of included organic materials. Deliberate designs such as cylindrical or conical holes are possible if formed before the ceramic is fired. Such a procedure would retain the desirable mechanical strength and support, and improve the permeability. By including an appropriate gas in the device the resulting ionization and space-charge neutralization could enhance the electron flow through porous media.

#### ASSOCIATION OF INSECTS WITH THE OAK TREE AND ENDOCONIDIOPHORA FAGACEARUM BRETZ<sup>1</sup>

Dale Melvin Norris, Jr.<sup>2</sup>

Department of Zoology and Entomology

The initial experimental demonstration that sap- and fungus-feeding insects can transmit Endoconidiophora fagacearum Bretz was first reported by Norris in 1953. Studies of the possible role of these insects in the spread of the fungus have continued. These investigations have dealt with the following three phases of the problem: (1) insects occurring on the fungus mats, (2) insects occurring in wounds on living oak trees, and (3) conditions conducive to this type of fungus spread.

As a result of the examination of some 1200 mats, 58 species of insects in seven orders and 21 families were observed. The dominant families in the order of their importance were Nitidulidae, Staphylinidae, Cucujidae, and Entomobryidae. The remaining families were of distinctly less importance.

In studies of the succession of insects coming to mats as the latter pass through their various stages of development, insects did not fall into clear-cut categories as to their total occurrence, but most of the more dominant species were distinctly more abundant during a definite mat developmental stage. Those species with their peak abundance occurring while ascospores were being produced were considered as the most likely vectors from the inoculum standpoint.

The percentage of observed mats bearing each species, and the species and total insect populations, were determined on examined mats during all months of the year. Thirteen species were distinct dominants of the total insect population from this viewpoint. Six of the 13 were nitidulids. The two most abundant species were Colopterus truncatus (Randall), and Tinotus imbricatus (Csy.)?.

<sup>1</sup>Doctoral thesis number 1767, submitted March 2, 1956. Chairman of Committee, H. M. Harris, Department of Zoology and Entomology.

<sup>2</sup>B.S., Iowa State College, Ames. M.S., *ibid*.

Graduate Assistant, Agricultural Experiment Station.

Through the examination of many injuries in living oak trees, 121 species of insects representing nine orders, 45 families, 89 genera, and 7 species undetermined to genus were observed. The major families in terms of number of species were Nitidulidae, Formicidae, and Staphylinidae. All other families were of minor importance from this standpoint. In terms of injuries susceptible to fungus infection, only 50 species were observed at Forest City, Iowa; and 70 at Lehigh, Iowa. Sixteen species were more abundant than the rest, and Tinotus sp. (probably) imbricatus was the most abundant.

In any interrelationship involving two or more organisms, as in the case of oak wilt, certain basic conditions are necessary in order for this relationship to be perpetuated. The three basic components were found to be the (1) inoculum source, the mat; (2) the entrance into the oak, the wound; and (3) the vector, the insect.

With regard to the inoculum source, only 45 of 496 oak wilt fungus isolation attempts from mat-inhabiting insects were positive. However, by inoculation of single contaminated insects into fresh wounds, 100 per cent of 15 C. truncatus beetles were shown to bear viable fungus. Such an insect was shown to be capable of feeding for a period of 24 hours on a sweet corn medium after fungus contamination and still retain enough inoculum to infect an oak through a fresh injury. Wilt only developed in trees whose fresh wounds were subjected to insects contaminated on ascospore-bearing sources. Mats bearing "fresh" ascospore-containing exudate were much more effective in the fungus contamination of insects than those bearing "old" exudate.

In considering wounds in oaks, three factors, (1) nature of wound, (2) season of the year, and (3) age of wound, were apparently most important in making an injury a suitable entrance for the fungus.

The major requirement as to the nature of the injury was that it must penetrate into the cambial region. The specific wounding agent was not important since isolated infections were associated with various causes of injury. Natural infection through experimentally inflicted wounds occurred only during April, May, and June in Iowa. The cessation of this period of infectability was closely correlated with the end of vigorous spring growth in oaks. The only wilt that developed in unwounded check trees was associated with fresh natural wounds. Infection never occurred through a wound that was more than two weeks old. Wounds were susceptible to only immediate inoculation during August.

The biological habits apparently necessary for an insect to serve as a vector of the fungus were investigated and those species fulfilling these established requirements were determined. Eighteen species were qualified, but seven were too rare to be of any significance. Of the remaining eleven species, five were nitidulids. The two best qualified species were Tinotus imbricatus? and Colopterus truncatus.

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ADJUSTMENTS TO IMPROVE INCOMES AND TO MEET CHANGES IN  
RELATIVE PRICES ON DAIRY FARMS IN NORTHEAST IOWA<sup>1</sup>Frank Orazem<sup>2</sup>

Department of Economics and Sociology

This study refers to 160-acre farms, the modal size in northeast Iowa. Optimum plans have been determined for farms with different amounts of operating capital and labor. Different livestock and cropping practices have also been considered.

The main objectives of this study were: (1) to determine the effects of a 20 per cent decline in the price of milk on the farm incomes as well as on the farm organizations; (2) to specify the adjustments farmers in northeast Iowa could make to offset decreases in income from lower milk prices considering different cropping and livestock alternatives of production; (3) to provide useful information to facilitate the process of adjustment for individual farmers and those counseling them on problems of adjustments; and (4) to provide guidance for those who must decide on future policies to be followed with respect to this area.

The linear programming analysis has been used as a tool for analyzing the production possibilities and adjustment problems for different farm situations considered in this study.

A 20 per cent decline in the price of dairy products would reduce farm income on a one-man farm on the average by 9.2 per cent. To offset this income decline from lower dairy product prices an individual farmer on a 160-acre one-man farm could either improve his cropping program, improve the production practices of livestock enterprises, or he could reorganize both his cropping and his livestock program.

The cropping pattern most desirable from the standpoint of the individual farmer on a one-man farm would be the CCOM rotation, with terracing applied where necessary to control erosion. The present cropping pattern which approximates a combination of corn-oats-meadow and corn-corn-oats-meadow-meadow rotations may be adequate for farmers who have access to a larger amount of labor and who can keep a dairy herd of the size that would utilize all the hay produced, or for farms of smaller size.

A change from the present cropping pattern to the CCOM rotation would increase income on a one-man farm with \$3,000 of operating capital--which is relatively limited and would not allow for any application of commercial fertilizer--by 14.3 per cent. It would increase farm net incomes on farms which can afford fertilizer application by 17.9 per cent. This increase in farm income from changes in the cropping program would be large enough to offset a 20 per cent decline in the price of milk mainly through increased production of corn, which can be either sold or fed to livestock. The present cropping program on a one-man farm produces an abundance of hay, more than the farmer can efficiently use with the assumed labor.

Also, improved production practices in livestock enterprises (dairy and hogs) would improve and offset the decrease in income. However, improved practices on the dairy enterprise alone would not make up for the loss in the farm's income if the price of milk declined by 20 per cent.

The optimum plans for the one-man 160-acre farms would remain diversified with either projected or 20 per cent lower milk prices. Hence the effects of changes in relative prices are less drastic in these plans than they

<sup>1</sup>Doctoral thesis number 1807, submitted June 2, 1956. Chairman of Committee, E. O. Heady, Department of Economics and Sociology.

<sup>2</sup>Dr. Sci. Pol., Karl Franzens University, Austria. M.S., Kansas State College, Manhattan. Graduate Assistant, Agricultural Experiment Station.

would be if farms specialized in dairying. A decline in dairy product prices would exert greater effects on incomes and on optimum organization on two-man farms than on one-man farms. However, not all of the farms would be affected equally.

If farmers on a two-man farm balanced their cropping and their livestock program with the rest of the farm resources, they could almost double the size of the dairy enterprise and expand their milk production even under less favorable milk prices. These adjustments alone, everything else being the same, would increase farm net incomes on an average of 20 per cent. Improved practices on the dairy enterprise would enable farmers in this group to increase their incomes by an additional 15.8 per cent.

These types of adjustments would reduce the per unit costs of producing milk and would be profitable, at least in the sense that individual farmers concerned would be financially better off primarily for having made them than they would be otherwise. These kinds of adjustments would provide a basis for a gradual change in dairying. They also appear to offer the main hope for reducing costs in milk production and for maintaining or improving net incomes on dairy farms in the years ahead even if prices decline by 20 per cent or more.

The result of improved dairy practices would be more milk on these farms and also in total unless offset by a reduction in milk output on other farms where operators could find better opportunities in other enterprises or in off-farm employment. These adjustments may, however, lay the groundwork for meeting the increased total demands for dairy and other agricultural products that are expected to develop as the population grows.

A change in the relative price relationships would also affect the land use pattern. In optimum plans where the dairy enterprise would decrease due to lower milk prices, the cropping program would shift from relatively more soil conserving rotations to relatively more soil erosive rotations. Hence, a decline in the price of dairy products would change the price ratios in favor of soil erosive crops.

To offset declines in income caused by decreases in milk prices the individual farmer in northeast Iowa would have to improve on his customary production practices and change his composition of output. Flexibility rather than rigidity within the farm organization will enable a farmer to make adjustments to price changes in order to maintain or improve his income.

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#### COUPLED NUCLEOSIDE PHOSPHORYLASE REACTIONS IN *ESCHERICHIA COLI*<sup>1</sup>

John L. Ott<sup>2</sup>

Department of Bacteriology

Cell-free extracts prepared from *Escherichia coli* formed ammonia from adenosine and to a lesser extent from adenine. When inosine was added with adenine, the formation of ammonia was stimulated to a marked degree. By the use of an adenosine deaminase (prepared from calf intestine and specific for adenosine), it was shown that adenosine was formed from adenine and inosine. The extract catalyzed the following reaction:

<sup>1</sup>Doctoral thesis number 1780, submitted March 30, 1956.

Chairman of Committee, C. H. Werkman, Department of Bacteriology.

<sup>2</sup>B.A., University of Kansas, Lawrence. M.A., *ibid*.  
Graduate Assistant, Agricultural Experiment Station.

(1) Adenine + Inosine  $\rightleftharpoons$  Adenosine + Hypoxanthine

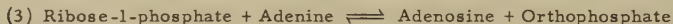
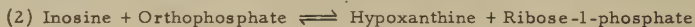
The adenosine deaminase in the extract of *E. coli* had its optimum activity at pH 8.0. It showed little activity at pH 6.5. The enzyme system that formed adenosine from adenine and inosine had its optimum activity at pH 6.5. Reaction (1) was studied at pH 6.5 to prevent the destruction of adenosine by deamination.

Methods were developed for the quantitative determination of the four compounds in reaction (1). The quantitative measurement was based on the absorbency of the compounds in the ultraviolet. The mixtures were separated by selective precipitation of the purine bases as silver salts, or by paper chromatography. The quantities of the separated compounds were determined spectrophotometrically.

The stoichiometry of the reaction was demonstrated. One mole each of adenine and inosine formed one mole each of adenosine and hypoxanthine. The reaction was shown to be reversible. The equilibrium constant and kinetics of the reaction were determined. With dialyzed extracts, it was shown that orthophosphate was required for the optimum rate of reaction; orthophosphate was not required in stoichiometric amounts. Certain divalent cations inhibited the reaction. This inhibition was overcome by the addition of orthophosphate.

The mechanism of reaction (1) may involve: (a) a transamination from adenine to inosine, or (b) to transfer of the ribosyl group from inosine to adenine. When reaction (1) was carried out with adenine-8-C<sup>14</sup> as one substrate and the compounds in the mixture separated by paper chromatography, all of the radioactivity was found in adenine and adenosine. Adenosine had essentially the same specific activity as adenine. Hypoxanthine and inosine were devoid of radioactivity. The mechanism of the reaction was established as a transfer of the ribosyl group, and transamination was eliminated as a possible mechanism.

The data from the tracer experiments did not establish a direct transfer of the ribosyl group from a nucleoside to the purine base. The same results would be obtained through a combination of the following reactions:



Phosphorolysis of adenosine and inosine was catalyzed by the cell-free extracts of *E. coli*. The reactions formed only small amounts of the purine bases. Ribose-1-phosphate was prepared from inosine, orthophosphate, cell-free extract of *E. coli*, and xanthine oxidase. Xanthine oxidase was added to remove hypoxanthine and force reaction (2) to the right. Ribose-1-phosphate was isolated as the barium salt. It contained ribose and acid-labile orthophosphate in equimolar amounts. Orthophosphate was split from the compound by hydrolysis at room temperature in 0.5 N HCl in 30 minutes. On the basis of ribose and acid-labile orthophosphate content the ribose-1-phosphate had a purity of 50 per cent. In the presence of cell-free extract, ribose-1-phosphate reacted with hypoxanthine to form inosine. Ribose-1-phosphate also reacted with adenine in the presence of enzyme to form adenosine. These data indicated that reactions (2) and (3) were catalyzed by the cell-free extract of *E. coli*. Coupled nucleoside phosphorylase reactions with ribose-1-phosphate as the intermediate was proposed as the mechanism for the conversion of adenine and inosine to adenosine and hypoxanthine.

The possibility of trans-N-ribosidation as a mechanism for reaction (1) was not eliminated. The presence of orthophosphate in the cell-free extracts after dialysis and the catalysis of phosphorolytic reactions by these extracts in the absence of added orthophosphate, indicated that the presence of trans-N-ribosidase need not be postulated to account for reaction (1). The demon-



stration of trans-N-ribosidase would require the preparation of extracts of *E. coli* that catalyze reaction (1) and are not affected by orthophosphate or the presence of ribose-1-phosphate. Such extracts were not obtained.

A role for the coupled nucleoside phosphorylase reactions in nucleic acid synthesis was proposed.

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## INTERRELATIONSHIPS OF LACTOSE, LIPIDS, AND MINERALS IN NUTRIENT UTILIZATION BY THE CALF<sup>1</sup>

Foster Gamble Owen<sup>2</sup>

Department of Animal Husbandry

The influence of various components of milk type diets on fecal characteristics and ration utilization has been studied in four phases. Preliminary tests involving 17 calves (4-120 days of age), in 177 individual trials, were made to obtain a general appraisal of the laxativeness of certain milk constituents. Assessments were made on the diarrheic effect of altering the composition of a whole milk diet (fed at 8 per cent of body weight per day) by doubling the lactose content (2X), increasing the lactalbumin content by 1 per cent, and increasing the mineral level from two to ten times (2X to 10X) with the addition of a simulated milk ash. Certain combinations of these ingredients were also tested. Effects were likewise obtained from supplementing reconstituted skimmilk (fed at 10 per cent of body weight) with butter oil (3 per cent), lactose (2X), and minerals (4X), individually and in various combinations. Tests were also made on the laxation from diets of lactalbumin, lactose, and minerals formulated to simulate whey product, which is consistently laxative in effect.

A study was made on curd formation and abomasal emptying time, using two calves with rumen fistulas through which the abomasum could be palpated. The effectiveness of sodium citrate, at various levels, as an anticoagulant was tested with these animals.

Eight calves were assigned at 11 days of age to a diarrhea experiment according to an 8 x 8 quasi-latin square design in order to more thoroughly test the effects of lactose (2X), minerals (4X), milk fat (3 per cent), curd formation, and the interactions of these factors. Raw skimmilk (or whole milk when testing fat), at 8 per cent of body weight daily, served as the basic diet. Test diets were fed for four-day periods followed by a minimal three-day recuperation period.

The final phase of this study involved the sacrifice of five calves which had, 14 hours previously, received a control (whole milk) diet and four calves which had received a diarrheic type diet (skimmilk, lactose (2X), and minerals (4X)). Chromic oxide was included in both type diets so that an evaluator could be made of its usefulness as a digestibility indicator under these conditions. Digestive tracts were segmented into five portions (stomach, anterior and posterior halves of the small intestine and anterior and posterior halves of the large intestine through which the test diet had traversed), the contents were collected and subjected to chemical and physical measurements.

Preliminary results indicated that neither minerals nor lactose, per se,

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<sup>1</sup>Doctoral thesis number 1768, submitted March 3, 1956. Chairman of Committee, N. L. Jacobson, Department of Animal Husbandry.

<sup>2</sup>B.S., Alabama Polytechnic Institute, Auburn. M.S., Iowa State College, Ames. Graduate Assistant, Agricultural Experiment Station.

had an appreciable laxative effect; however, the two in combination consistently (except with whole milk) produced moderate to severe diarrhea. Lactalbumin supplementation of whole milk had no effect on diarrhea, but reconstituted diets containing lactalbumin or casein produced results which varied from cases of definite looseness to no effect. The lactalbumin-containing diet was similar in composition to whey product, which consistently produced severe diarrhea.

In order to test the influence of curd formation on diarrhea a means was devised in which sodium citrate addition to the milk eliminated curd formation. Abomasal emptying time averaged 14 hours for curd producing milks and less than one hour for noncoagulating milks.

It was concluded from the diarrhea experiment in which 16 diets were tested that minerals were the main factor in provoking diarrhea, fat had an over-all antidiarrheic action, and lactose appeared to be a possible cause of laxation. Neither curd formation nor any of the two- or three-way interactions seemed to be concerned in fecal consistency.

Analysis of the contents in the various segments of the gut of the animals that were sacrificed revealed no appreciable differences between diets in pH values, the total apparent recovery of the total liquid, dry matter, or carbohydrate fed, and the total amount of lipid in the tract. The digestive tracts of calves fed the diarrheic type diet, as compared to those of the control calves, contained about 15 per cent of the dietary protein, about 50 per cent more total ash and 2.5 times as great a ratio of nonprotein nitrogen to protein nitrogen in the posterior half of the small intestine.

The normal condition in the digestive tract of calves after about 14 hours digestion of a milk diet is represented by the findings in the control calves. pH values were: stomach 5.65; anterior and posterior portions, respectively, of the small intestine, 6.65 and 7.31; and anterior and posterior portions, respectively, of the large intestine through which the test meal had passed, 7.14 and 7.06. At the time of slaughter the nutrients of the diet had apparently been absorbed to the extent of 64 per cent for dry matter, nearly 100 per cent for the carbohydrate, 80 per cent for the lipid and 34 per cent for the protein. About 11 per cent more mineral was recovered than fed. Chromic oxide seemed to have settled in the folds of the digestive tract and did not show a smooth trend toward concentration in its transit of the digestive tract. It was concluded, therefore, that chromic oxide is unsuitable for use as digestibility indicator for milk-fed calves.

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#### COMPARATIVE HISTOCHEMICAL STUDIES ON THE ENDOGENOUS STAGES OF *EIMERIA TENELLA* AND *E. NECATRIX*<sup>1</sup>

Walter Hugh Pattillo<sup>2</sup>

Department of Zoology and Entomology

An investigation was carried out on some of the histochemical reactions shown by *Eimeria tenella* and *E. necatrix*, the two coccidia which produce the most severe pathological conditions in the intestines of the chicken. It was hoped that a study of these severely pathogenic types might expose important differences between the physiological processes displayed by them and the

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<sup>1</sup>Doctoral thesis number 1803, submitted June 1, 1956. Chairman of Committee, Elery R. Becker, Department of Zoology and Entomology.

<sup>2</sup>B.S., Hampton Institute, Hampton, Virginia. M.S., Iowa State College, Ames. Graduate Assistant, Industrial Science Research Institute.

less pathogenic forms previously studied. The reactions of E. tenella and E. necatrix were compared, because the stages of these parasites producing extreme pathologic effects occur in different sites in the intestinal tract. The effects of sulfaquinoxaline therapy upon the histochemical reactivity of E. tenella was also studied. Certain other problems concerning the life cycle of E. tenella were investigated.

Glycogen was identified by the periodic acid-Schiff (PAS) reaction and the combined PAS-Feulgen reaction in conjunction with diastase- or alpha-amylase-treated controls. Acid mucopolysaccharides were distinguished by their metachromatic properties when stained with toluidine blue. Reaction to the enzymes hyaluronidase, beta-glucuronidase, alpha-amylase, beta-amylase and ribonuclease, and to toluidine blue-staining at low pH's were used to further characterize the acid mucopolysaccharides. The Feulgen reaction for deoxyribonucleic acid (DNA), the ribonuclease-toluidine blue test for ribonucleic acid (RNA), and the mercuric-bromphenol blue test for proteins were employed. The oil soluble dyes Sudan Black B and Sudan IV were used to identify lipids in cecal smears of E. tenella infections, and a modified Ciaccio procedure was employed on tissue sections.

Glycogen was observed in varying amounts in all stages of E. tenella and E. necatrix. Sporozoites, second generation trophozoites, and nearly mature second generation schizonts, as well as macrogametocytes and oocysts, contained large amounts of it. Nearly mature and mature first generation schizonts and merozoites, third generation schizonts and mature microgametocytes contained lesser amounts of glycogen. Sporozoites of E. tenella, identified by their cytoplasmic glycogen, were observed invading the surface epithelium of the ceca through "penetration tubes." They crossed the basement membrane which acted as a temporary barrier, migrated through the tunica propria, and invaded the glandular epithelium. First generation merozoites invaded the glandular epithelium and formed second generation trophozoites which contained an enlarging mass of glycogen. These parasitized glandular cells enlarged and passed into the tunica propria. While the developing second generation parasites contained little glycogen, a sudden increase occurred as maturity approached.

The peripheral granules of the macrogametocytes and the oocyst walls gave positive PAS reactions for a polysaccharide which was not affected by incubation in diastase, alpha-amylase, beta-amylase, hyaluronidase or by extraction with hot methanol:chloroform. Acetylation prevented the PAS reaction in these granules. They gave intense protein reactions, but no lipid reactions. The oocystic wall was derived from these granules.

An acid mucopolysaccharide was present as metachromatic granules in all stages of both species except maturing macrogametocytes and oocysts. The second generation schizonts contained the largest quantities.

DNA was found in all stages except in the macrogametocytes. RNA as well as protein was present in large quantities in all actively growing stages and in lesser amounts in other stages. The refractile globules of the sporozoites gave intense protein reactions.

Neutral fats were identified in large quantities in the second generation parasites, macrogametocytes, and oocysts of E. tenella. Certain lipids, resistant to fat solvents when chromated, were observed in varying amounts in all stages of the parasite. The refractile globule of E. tenella sporozoites gave a strongly positive lipid reaction.

Sulfaquinoxaline affected the histochemical reactions of E. tenella. The distribution and morphological character of glycogen were disturbed in a few first generation schizonts and in the majority of the second generation schizonts. The effect on the acid mucopolysaccharide was not clear. DNA synthesis and nuclear division were retarded, although a few schizonts produced abnormal merozoite-like bodies. Noticeable decreases in the RNA and protein content of schizonts were observed. Karyosomes increased beyond

their normal size. No great decrease in the quantity of lipid was noted, although its appearance and distribution were altered in many instances. The lipid globules in the host cells of the parasites increased in size.

While the reactions shown by *E. tenella* and *E. necatrix* were basically alike, the main differences between these coccidia and the less pathogenic ones studied previously were in the large amounts of glycogen, fats, and acid mucopolysaccharides in the asexual stages of the former. It was suggested that the glycogen and fats are utilized as energy sources, and that the acid mucopolysaccharides serve in a protective capacity.

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## FRAME CONSTANTS FOR A WOODEN BUILT UP GIRDER<sup>1</sup>

John H. Pedersen<sup>2</sup>

Departments of Agricultural Engineering and of Civil Engineering

The primary purpose of this work was to determine the frame constants for built up wooden open web girders composed of two horizontal parallel chords with vertical rigidly connected web members. Secondary considerations included development of a design procedure and discussion of fabrication methods and potential applications.

Empirical values were obtained for the frame constants by reproducing in the laboratory the conditions assumed in each of the various steps of the moment distribution method of rigid frame analysis. Models of 24-foot span were tested for three levels of web spacing (one-fourth, one-eighth, and one-sixteenth of the span), and four levels of member size (nominal 2 x 4 in., 2 x 6 in., 2 x 8 in., and 2 x 10 in.). The depth of the girders was fixed at one-twelfth of the span. The chords were composed of a single member, nominally 2 in. thick; the webs were composed of two members, one nailed and glued to each side of the chords, nominally 1 in. thick and with a width equal to that of the chords.

The girders were incorporated into rigid U frames by gluing and bolting columns (composed of two members the same size as the chords) to the ends of the girders. Roof loads were based on the assumption that purlins would extend between the U frames and would be spaced at one-half of the web spacing.

For the determination of the stiffness and carry-over factors, a moment was applied to one end of the girder with a couple and the resulting angle change measured, and sufficient moment was applied to the other end to prevent it from rotating. For the determination of fixed end moments a series of concentrated loads was applied to the upper chords, and end moments applied sufficient to prevent angle change at both ends of the girder.

Each of the frame constants was found to increase with a decrease in web spacing and an increase in member size. The empirical frame constants were presented graphically in dimensionless form.

The effective moment of inertia for use in the preliminary design of girder size was computed from the empirical stiffness factors and the definition of the stiffness factor for a member of uniform moment of inertia and modulus

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<sup>1</sup>Doctoral thesis number 1735, submitted December 1, 1955. Chairmen of Committee, Henry Giese, Department of Agricultural Engineering, and C. A. Caughey, Department of Civil Engineering.

<sup>2</sup>B.C., Cornell University, Ithaca, New York. M.S., Iowa State College, Ames. Associate, Agricultural Experiment Station.

of elasticity. Analytical effective moments of inertia were derived from an approximation of the elastic behavior of the girders and were found to approach the experimental values for the more rigid girders.

The frames into which the girders had been incorporated were loaded with concentrated loads simulating purlin loads, and the resulting horizontal thrusts at the hinged column bases measured. These thrusts were compared with thrusts obtained from the experimental effective moments of inertia and found to be in close agreement. They were further compared with thrusts obtained from a moment distribution solution of the frames using the empirical frame constants and were found to be in close agreement for the more rigid girders. Deformation, which was not reflected in the frame constants, in the portion of the lighter columns between the chords induced larger thrusts than were predicted from use of the frame constants. This deformation, and failures in the webs during ultimate load tests, indicated that additional resistance to horizontal shear is required in the lighter girders.

A design procedure was developed which included a method of determining the required size of plywood plates to be inserted between the column and chord members to increase the horizontal shear resistance of the girders and reduce deformation in the columns.

Difficulty was encountered in developing good glue bond in cup warped members of nominal 2-inch material. Relative placement of cup warped surfaces, in addition to size and placement of bolts, was found to be critical in glued and bolted joints.

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## CORRELATION OF SELECTED SOIL INDICES WITH PLANT GROWTH ON HIGHWAY BACKSLOPES<sup>1</sup>

Paul Peperzak<sup>2</sup>

Department of Agronomy

In an attempt to evaluate and analyze the problem of backslope revegetation, a survey was made of backslope exposures along about 3500 miles of highways in the State of Iowa. A selected number (55) of road cuts, exhibiting distinct differences in vegetation among the various zones within the same slope, were studied in greater detail.

Plant growth was measured on 241 selected sampling sites by the total dry weight of plant clippings on each site. Soil samples, taken from the same sites, were morphologically described and analyzed on 20 different soil properties.

A description of backslope materials of major occurrence, classified as to geological strata, was made on the basis of analytical data and color determinations. A further separation within till and loess materials was made according to the degree of weathering to which the materials had been subjected.

Division of all observations on each measured soil index into interquartile intervals made calculation of association chi-squares possible. Chi-square values give a measure of the closeness of association between two variables and indicate the sign of the expected correlation between the same factors.

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<sup>1</sup>Doctoral thesis number 1781, submitted March 30, 1956.

Chairman of Committee, W. D. Shrader, Department of Agronomy.

<sup>2</sup>B.S., Agricultural University, Holland. M.S., Ingenieur, *ibid.* M.S., Iowa State College, Ames. Graduate Assistant, Agricultural Experiment Station.



Multiple regression statistics were finally calculated for 12 of the original 20 soil indices.

Plant yields did not seem to be greatly influenced by geographic and climatic location or aspects of exposures. Plantings made during or before 1953 appeared to be significantly different from those made after 1953. Variations within plant yields from exposures planted before 1953 were not large enough to warrant separation by year of planting. A fairly homogeneous population of observations was therefore obtained after the elimination of samples collected from backslopes planted later than 1953.

The chi-square analysis on the associations between yields and soil factors and among soil factors demonstrated that 12 of the 20 soil factors were significantly associated with yields. They were: clay content, aggregation, wilting point, moisture equivalent, aeration porosity, capillary porosity, initial nitrate, nitrifiable nitrogen, available phosphorus, available potassium, cation exchange capacity, and total exchangeable bases.

For a good understanding of all the associations and of some of the seemingly contrary results obtained in the analysis, an explanation was given of a priori expected, causal effects, and correlations among factors and yields. This was illustrated by a specially constructed diagram. Chi-square analysis further revealed that most of the soil properties were highly intercorrelated and that many of the correlations were largely determined by extreme textural conditions, caused especially by high clay contents. The true effect of various soil factors seemed to be obscured by these mutual associations with clay content. A subsequent separation of all observations on the basis of clay content resulted, therefore, in the formation of two distinct populations each with its own specific regression parameters.

On the basis of the chi-square analysis, several soil factors could be eliminated from further statistical analysis as information given by these factors with respect to plant growth seemed to be duplicated by other factors in a more efficient manner. Total porosity was thus replaced by capillary porosity; pH by exchangeable hydrogen; and both total exchangeable bases and percentage base saturation by cation exchange capacity.

Correlation coefficients calculated in the course of the multiple regression analysis on the two separate populations showed similar correlations among factors as obtained in the chi-square analysis. However, only four significant partial regression coefficients were obtained in each of the two sets of observations. In the materials low in clay, nitrifiable nitrogen and available phosphorus have a definite positive effect on plant yields as shown by their positive regression coefficients; however, sand content and exchangeable hydrogen decrease yields. Variation of plant yields, explained by multiple regression, was in this case 32 per cent.

In the set with clay-rich materials, nitrifiable nitrogen and initial nitrate had significant positive regression coefficients, while sand content and capillary porosity had negative regression coefficients. Variation explained by multiple regression in this set was 46 per cent.

Deletion of the eight remaining soil factors, which had failed to attain significant values in their partial regression coefficients, reduced the total information from 32 to 26 per cent in the first set and from 46 to 38 per cent in the second.

The practical implications of this study are that adequate fertilization, usually in the form of nitrogen and phosphorus, and structural improvements, by way of cultivation, mulching, and top-soiling, are necessary for the establishment of a satisfactory vegetative cover on highway backslope exposures.

More research needs to be done in finding suitable and adequate measurements of soil properties which may expect to influence plant growth positively. Fertilizer experiments on backslope materials in the field may be expected to yield more detailed information on the nutrient requirements of these materials.

PHASE STUDIES OF URANIUM-ZIRCONIUM ALLOYS<sup>1</sup>David Peterson<sup>2</sup>

Department of Chemistry

The uranium-zirconium phase system was studied and a phase diagram was proposed. Methods of preparing alloys of uranium with zirconium were investigated and an attempt was made to evaluate the applicability of the various methods. The hardness of these alloys of uranium and zirconium was measured and their ability to undergo mechanical working was investigated.

Alloys of uranium with zirconium were prepared by bomb reduction of uranium tetrafluoride and zirconium tetrafluoride in dolomitic oxide crucibles and in graphite crucibles. Metallic calcium was used as the reductant and iodine was added as a booster. Alloys of uranium with zirconium were also prepared by other methods such as powder metallurgy, vacuum melting uranium with zirconium in graphite crucibles and arc melting uranium with zirconium.

The alloys were studied by thermal methods, by microscopic examination, and by X-ray diffraction. Thermal analysis curves, which proved to be useful in determining the solid state transition temperatures were run by in a constant temperature differential apparatus. The liquidus and solidus temperatures were investigated by measuring, with an optical pyrometer, the temperature at which the first sign of melting was observed. This temperature must be above the solidus temperature and below the liquidus temperature. Microscopic examination of slow cooled and of quenched samples was used to determine the number of phases which were present and the extent of the various phase regions. The phases which were present were identified by their X-ray diffraction powder patterns.

The solidus and liquidus lines in this phase diagram have no maximum, minimum, or horizontal portion. A continuous solid solution exists between gamma uranium and beta zirconium. The solubility of zirconium in alpha uranium was established as less than 0.6 per cent at 579°C and the solubility in beta uranium is less than 1.2 per cent at 694°C. The beta-gamma transition is lowered to 683°C by the addition of zirconium and the alpha-beta transition is raised to 683°C at 1.9 per cent zirconium. A eutectoid transformation at that temperature was observed up to 30.1 per cent zirconium. The solubility of uranium in alpha zirconium is probably between 2.3 and 4.4 per cent uranium at 580°C. A thermal arrest was observed at 605°C which was interpreted as being due to a eutectoid in the system at that temperature arising from the alpha-beta transition in zirconium. X-ray diffraction data indicated that both alpha uranium and alpha zirconium were present in slow cooled and quenched alloys containing from 30 per cent to 70 per cent zirconium.

<sup>1</sup>Doctoral thesis number 1143, submitted December 16, 1950.

Chairman of Committee, Harley A. Wilhelm, Department of Chemistry.

<sup>2</sup>B.S., Iowa State College, Ames. Junior Chemist, Institute for Atomic Research.

SEPARATION OF HAFNIUM AND ZIRCONIUM BY  
LIQUID-LIQUID EXTRACTION<sup>1</sup>Howard Carl Peterson<sup>2</sup>

Department of Chemical Engineering

A liquid-liquid extraction process has been developed which produced an aqueous solution of zirconium nitrate containing less than 100 parts of hafnium per million parts of zirconium. An aqueous solution of zirconium and hafnium nitrate-nitric acid was contacted with tributyl phosphate organic solvent in a 14-stage mixer-settler apparatus. The zirconium was preferentially extracted into the organic solvent. The hafnium and a majority of the minor impurities remained in the aqueous phase. The zirconium in the organic solvent was removed from the solvent with distilled water in a second mixer-settler apparatus. The recovery of hafnium-free zirconium was greater than 96 per cent.

The source material for zirconium was the reaction product of caustic soda and zircon sand. The reaction product was leached with water to remove the water soluble silicates and then was dissolved in sulfuric acid. The zirconium was precipitated as zirconium hydroxide from the zirconium sulfate solution by the addition of ammonium hydroxide. The sulfate was then washed from the hydroxide and the washed hydroxide was dissolved in nitric acid. This procedure was effective in reducing the silica content of the nitrate solution to the very low levels necessary for trouble-free extractor operation. The dissolution of the leached reaction product in nitric acid and hydrochloric acid was also studied.

In the separation of zirconium from hafnium by extraction, an organic solvent of 60 volume per cent tributyl phosphate-40 volume per cent heptane was used. The combination of 5.0 normal nitric acid aqueous solutions and the 60-40 solvent mixture was determined the optimum from mass transfer, separation, and solvent degradation considerations.

A procedure to obtain equilibrium data and to predict continuous operation in fractional liquid-liquid extraction was presented. Preliminary equilibrium data were obtained from a simulated column run, involving a series of batch contacts operated in such a manner as to approach steady state counter-current extraction. The flow ratios and stage requirements for a continuous run were then determined by trial and error using the modified McCabe-Thiele method. The use of the procedure was successful in predicting product composition in continuous extraction runs.

A preliminary cost analysis indicated a chemicals cost of \$0.99 per pound of hafnium-free zirconium, for converting zircon sand into a hafnium-free solution of zirconium nitrate. A similar figure for the currently used thiocyanate extraction process is \$1.34.

<sup>1</sup>Doctoral thesis number 1456, submitted August 7, 1953. Chairman of Committee, G. H. Beyer, Department of Chemical Engineering.

<sup>2</sup>B.S.E., University of Michigan, Ann Arbor. M.S., Iowa State College, Ames. Graduate Assistant, Institute for Atomic Research.

DESIGN AND ANALYSIS OF ONION STORAGE TRIALS<sup>1</sup>Robert LeRoy Plaisted<sup>2</sup>

Department of Horticulture

This problem was designed to obtain information on methods of setting up onion storage trials and the analysis of the data obtained from them. A storage trial was run two years, and during the last year at two locations, one designed for onion storage and the other the basement of the horticulture building where the temperatures were high and the humidity low. The experiment was designed as a split plot with size of sample as the main plot and varieties as the subplot. Three sizes of sample, 25 bulbs, 50 bulbs, and 100 bulbs, and four varieties were used. Storage records were taken at monthly intervals during the last part of the storage period.

All analyses were computed both on the basis of percentage weight loss and on the percentage transformed to angles by the arc sine transformation. Both sets of data were subjected to tests for nonhomogeneity of variances and nonadditivity, and to a test to differentiate that part of the variance which is binomial.

In addition, tables are presented which make it possible to estimate the number of replications required to detect differences of varying magnitudes at several levels of probability of nondetection. Figures are presented which show the association of the error variances and the means for both the percentage and transformed data.

It would be to the advantage of the onion breeder to be able to accelerate his storage losses to obtain his storage information earlier. One procedure would be to use less than optimum storage conditions. The data at hand do not recommend such a practice since there exists a large variety by location interaction. The effect of changing storages is not one merely of acceleration. Thus it appears necessary to select a storage comparable to those in use by the growers for whom the hybrids are being developed. Another procedure proposed for obtaining storage information earlier, is merely to take the data earlier in the season. Here again, this is complicated by a large variety by length of storage interaction. Thus the length of storage should be conditioned by the length of time the growers usually like to store their crop.

Size of sample apparently has some effect on storage life both as a main effect and as an interaction with variety, but these effects are small and inconsistent. Any deviations from a common sample size in the range of 25 to 100 bulbs probably would not seriously affect any interpretations made by different breeders, particularly when the same hybrids are tested.

Any general statements concerning numbers of replications are difficult to make. Two standards of comparison, for example, are (a) four replications of 25-bulb samples analyzed as per cent loss should be expected to detect differences of 30 per cent of the mean in eight out of ten trials, and (b) to detect a difference of 10 per cent of the mean in eight out of ten trials one should have eight replications of 100-bulb samples and analyze the transformed data. The preceding estimates are based on the assumption that data were taken when the over-all mean percentage loss is somewhat over 50 per cent. Since the efficiency of estimating differences increases concurrently with increasing size of sample and prolonged storage and is closely associated with the over-all mean per cent loss, the tables given in the text of the thesis should be consulted to obtain information on different sets of circumstances of storage and assumptions of likelihood.

<sup>1</sup>Doctoral thesis number 1782, submitted April 4, 1956.

Chairman of Committee, E. P. Lana, Department of Horticulture.

<sup>2</sup>B.S., Cornell University, Ithaca, N. Y. M.S., Iowa State College, Ames.

The transformation of the percentage data to the arc sine reduced the non-homogeneity and nonadditivity of the variances found in the percentage data. The most benefit was derived for those analyses where one or more of the varieties' mean per cent loss fell outside a range of 30 to 70 per cent. Data of this sort should certainly be transformed, not only to more adequately meet the assumptions of the analysis of variance, but also to increase the efficiency of estimates of differences of the means.

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### VARIATIONS IN FOREST-DERIVED SOILS FORMED FROM KANSAN TILL<sup>1</sup>

Robert C. Prill<sup>2</sup>

Department of Agronomy

A field and laboratory study was made of the variations in the forest-derived soils formed from Kansan till.

Field studies included general field observations and the preparation of very detailed soil maps for two selected sites. As a result of these field studies five distinct variations in the forest-derived soils formed from Kansan till were recognized. These variations were designated as Lindley variants A, B, C, D, and E. Lindley variants A and B were observed to occur on the ridges and uppermost slopes with a slope gradient of 5 to 10 per cent. These variants A and B had a ferretto zone, a pebble band in the upper part of the ferretto zone and a till-like material or sediment above the pebble band. Variant A had a thicker zone of pedis sediment than variant B. Variant C with a slope range of 12 to 15 per cent occurred in a topographic downslope from variants A and B. Variant C had a pebble band at or near the surface and a ferretto zone which was not as red in hue or as heavy in texture as the ferretto zone in variants A and B. Variant D with a slope range of 17 to 25 per cent was observed to occur in a slope position downslope from variant C. Variant E with slopes up to 30 per cent was observed to occur generally downslope from variant D. Variants D and E did not have ferretto zones. Variant E was similar morphologically to variant D except that it was calcareous within 24 inches.

Morphological descriptions and laboratory data for ten profiles were obtained. Seven of these profiles represented variants observed in the Lindley series and three of the profiles were buried soils which contained a ferretto zone, a pebble band in the upper part of the ferretto zone, and a till-like material above the pebble band.

Results from particle size analysis indicated the till parent material for the profiles collected varied from 22 to 36 per cent in clay content.

The ferretto zone which was present in several of the profiles collected, ranged from 37 per cent to 65 per cent in clay content. A relationship of color of the ferretto zone to clay content was observed with the ferretto zones with the higher clay contents having colors redder in hue. Free iron content values obtained for the ferretto zones did not indicate any relationship between clay content and free iron content.

The cation exchange capacity showed a close relationship to the per cent

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<sup>1</sup>Doctoral thesis number 1710, submitted August 11, 1955.

<sup>2</sup>Chairman of Committee, F.F. Riecken, Department of Agronomy.

<sup>2</sup>B.S., Michigan State University, East Lansing. M.S., Iowa State College, Ames. Associate, Agricultural Experiment Station.



of less than 2 micron clay agreeing with data reported by other writers that the types of clay minerals in these Lindley variants are likely similar.

Results from studies on exchangeable potassium and potassium released from nonexchangeable form by extraction with 1.0 N HNO<sub>3</sub> showed that the forest-derived profiles developed from Kansan till are low in exchangeable potassium and potassium reserves having values comparable to Wisconsin till-derived soils.

The morphological, physical, and chemical properties of the Lindley variants showed a range in properties. This range being somewhat comparable to the range in properties observed for Gray-Brown Podzolic soils in Iowa formed from Wisconsin till and loess.

The Lindley variants were considered to be Gray-Brown Podzolic soils and to range in their degree of development from minimal to maximal Gray-Brown Podzolic soils.

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#### NEED FOR PANTOTHENIC ACID AND ITS RELATION TO ASCORBIC ACID IN NUTRITION OF THE GUINEA PIG<sup>1</sup>

Cecelia Dolores Pudalkewicz<sup>2</sup>

Department of Food and Nutrition

Two objectives were proposed for the present investigation regarding the need for pantothenic acid and its relation to ascorbic acid in the nutrition of the guinea pig. The objectives were (1) to produce a pantothenic acid deficiency in the guinea pig in two ways, namely, by feeding an antimetabolite, omega-methylpantothenic acid, and by omitting the vitamin from the diet, and (2) to determine whether an interrelationship between pantothenic acid and ascorbic acid existed in this species similar to that reported in the rat. Daft reported that when weanling rats were fed a pantothenic acid-deficient diet supplemented with 2 per cent ascorbic acid, they showed either no pantothenic acid deficiency symptoms, or the symptoms were greatly modified. Growth was better, porphyrin accumulation on fur and whiskers less, and length of life increased.

In Experiment A, nine pairs of weanling male guinea pigs were fed a complete basal diet consisting of rabbit pellets, supplemented with 10 mg ascorbic acid per day and one drop of oleum percomorphum per week. One pig of each pair was fed the complete basal diet with supplements and designated the control. The other pig of each pair was fed the basal diet and supplements with the addition of the antimetabolite, omega-methylpantothenic acid, as 0.15 per cent of the diet for 15 days, followed by 0.30 per cent for 18 days, and then 0.40 per cent for the remaining 14 days of the study.

After 15 days on 0.15 per cent analogue, three experimental animals and their litter mate controls were sacrificed. Up to this time, the experimental group was eating an average of one gram more food per day but gaining 0.9 gram less weight each day than the controls. No differences were observed between the two groups in red blood cell counts, packed red cell volumes, hemoglobin levels of blood pyruvic acid levels. However, the concentration of ascorbic acid in the blood serum of the experimental pigs was only one-half that of the controls.

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<sup>1</sup>Doctoral thesis number 1727, submitted October 31, 1955. Chairman of Committee, Charlotte E. Roderuck, Department of Food and Nutrition.

<sup>2</sup>B.S., Villa Maria College, Erie, Pa. M.S., Pennsylvania State University, University Park. Graduate Assistant, Agricultural Experiment Station.

When the experiment was terminated, after 47 days, the experimental animals were anemic, had serum ascorbic acid levels averaging one-half that of the controls, and showed an accumulation of pyruvic acid in the blood. As the level of analogue was increased, the differences in food intake, weight gain, and food efficiency between the two groups increased also. After 18 days on 0.30 per cent intake of analogue, the experimental pigs were gaining 3.4 grams per day less weight, eating two grams per day less food and utilizing their food less efficiently than the control group. After 14 days on 0.40 per cent intake of analogue, the difference between the two groups increased to 7.1 grams per day in weight gain and 11 grams per day in food intake.

Except for the decreased concentrations of ascorbic acid in the blood serum, the symptoms which were produced by feeding the analogue in this study, have been reported for one species or another as pantothenic acid deficiency. Physical symptoms observed in this experiment included soft woolly fur, pallor, lassitude, salivation, watering of the eyes, muscular weakness of the hind legs, convulsions, and coma. Biochemical changes were characterized by anemia, accumulation of pyruvic acid in the blood, and lowered serum ascorbic acid levels. Fatty livers and kidneys, hemorrhagic adrenals, and splenomegaly were observed upon autopsy.

In Experiment B, young male guinea pigs were fed a complete semi-synthetic ration along with four levels of ascorbic acid (0, 2, 10, and 40 mg per day) and four levels of calcium pantothenate (0, 0.06, 0.2, and 8 or 1 mg per day) in order to produce a pantothenic acid deficiency and to find whether or not an interrelationship existed between the two vitamins in the guinea pig.

The experiment was carried out in three separate studies. In Study I the animals ranged in weight from 91 to 210 grams and were maintained on the experimental regimen for eight weeks; in Studies II and III, two to four-day-old guinea pigs, ranging in weight from 68 to 113 grams, were maintained for four weeks.

The concentration of ascorbic acid in both the blood plasma and the adrenal glands reflected the dietary intake of the vitamin. Hypertrophy of the adrenal glands occurred in guinea pigs with scurvy, especially when the condition was chronic, and in pigs fed the pantothenic acid deficient diet especially when symptoms of pantothenic acid deficiency were also observed. Levels of pantothenic acid in the blood, in the liver, and in the urine seemed to reflect the dietary intake of calcium pantothenate. However, relatively large amounts of pantothenic acid were excreted in the urine of animals getting no dietary calcium pantothenate. The vitamin undoubtedly became available to the pigs through intestinal synthesis and coprophagy. Blood pyruvic acid levels showed no correlation with concentration of pantothenic acid in the blood.

It is believed that an acute deficiency of pantothenic acid was produced in two animals, while inanition probably complicated the symptoms suggestive of a pantothenic acid deficiency which were observed in two others. Symptoms included a soft woolly fur, lassitude, diarrhea, convulsions, and hemorrhagic adrenals. Anemia and a decrease in plasma ascorbic acid level were not found. Fatty livers occurred in pigs fed excessive amounts of calcium pantothenate.

Large amounts of calcium pantothenate failed to alleviate the symptoms of scurvy and large amounts of ascorbic acid did not prove beneficial in pantothenic acid deficiency; neither did large amounts of either of the two vitamins have any effect on weight gain, food intake, or food efficiency.

In conclusion, a pantothenic acid deficiency was produced in guinea pigs by feeding an antimetabolite with a natural ration, and by omitting pantothenic acid from a semi-synthetic diet. The deficiency, in the first case, was believed to have been chronic, in the latter case, acute. No clear-cut interrelationships between ascorbic acid and pantothenic acid were observed.

REACTIONS OF CERIUM AND LANTHANUM WITH CERAMIC OXIDES<sup>1</sup>George R. Pulliam<sup>2</sup>

Department of Ceramic Engineering

In this study the surface properties of cerium and lanthanum metals were determined for the metals melted on refractory oxide plaques of alumina, beryllia, thoria, and stabilized zirconia. The reactions occurring at the interface between the metals and the refractories were also determined by metallographic and X-ray techniques. The surface tension, contact angle, and work of adhesion were determined at temperatures of 810, 900, and 1000°C for cerium, and at temperatures of 950, 1000, 1100, and 1200°C for lanthanum. The metallographic examination of the reactions was conducted on polished sections of the interfaces. The temperatures to which the specimens were subjected for this phase of the study were 1100°C for cerium and 1200°C for lanthanum. To aid in the microscopic examination of the reactions between cerium and the oxides, mixtures of metal and ceramic powders were heated to temperatures of 500 and 804°C for cerium. Lanthanum and oxide powders were given a similar treatment to temperatures of 600 and 924°C. X-ray diffraction patterns of the mixtures were then obtained for the identification of the phases produced from the reactions.

The surface properties of the metals melted on the ceramic oxides were established by the sessile drop method of determining surface tension. The characteristic dimensions of the drop were obtained from photographs of the profile of the drop. The equilibrium between the known force of gravity acting on the drop and the unknown surface tension could be determined from the shape assumed by the drop. The dimensions obtained from the profile were used also to determine the contact angle displayed between the surface of the drop and the ceramic supporting plaque. The work required to remove the metal from the ceramic was then determined from the contact angle and surface tension from a consideration of the surface forces operative at the point of contact between liquid and solid plaque.

The surface tension determined by the sessile drop method is of reasonable accuracy only when the angle of contact of the surface of the drop with the supporting plane, is greater than 90°. For this reason the surface tension of lanthanum was determined from the run on zirconia. At a temperature of 950°C the surface tension of lanthanum was determined to be 710 dyne/cm  $\pm$  5%. The surface tension of lanthanum went through values of 693, 648, and 630 dyne/cm as the temperature of measurement became 1000, 1100, and 1200°C. The surface tension of cerium was determined from runs of the metal melted on beryllia and zirconia. At temperatures of 810, 900, and 1000°C the surface tension of cerium was determined on zirconia to be 695, 680, and 666 dyne/cm, respectively. At the same temperature the surface tension of cerium was determined on beryllia to be 740, 697, and 678 dyne/cm, respectively.

The contact angles of both metals were at their highest values when melted on zirconia. The contact angle of lanthanum on the oxides then decreased in the order: alumina, beryllia, and thoria. Cerium metal showed a very high contact angle with beryllia also, but the contact angle of cerium on thoria was assumed to be zero since the metal completely dissolved in the plaque. The rapid attack of alumina by cerium prevented measurement of the contact angle.

<sup>1</sup>Doctoral thesis number 1686, submitted June 20, 1955.

Chairmen of Committee, Morton Smutz, Department of Chemical Engineering, and C. M. Dodd, Department of Ceramic Engineering.

<sup>2</sup>B.S., Iowa State College, Ames. Research Assistant.

The work of adhesion of the metals to the oxides varied considerably between the metals and with the oxide studied. With both metals the work of adhesion was at a minimum for the melts on zirconia. The work of adhesion of the metals to thorium was by far the highest of all the oxides studied.

The work of adhesion of lanthanum to alumina and beryllia was intermediate between the adhesion to zirconia and thorium. The adhesion of cerium to beryllia, though not as low as the adhesion to zirconia, was lower than the adhesion of lanthanum to any of the oxides.

In general the interfacial reactions occurring between the metals and the oxides resulted in simple reduction of the oxides. Alumina was reduced by the metals to form the oxides of the molten metals and the alloys of aluminum and the metals. Beryllia was reduced in a similar fashion; however, alloying of the metals with beryllium did not occur. The metals reacted with zirconia to produce both an interfacial layer of the metal oxide and a limited solid solution of metal and zirconia. Both metals produced solid solutions with thorium.

The values determined for the surface tensions of cerium and lanthanum revealed the similarity that was to be expected from the similarity of the other properties of the metals. The value of surface tension decreased linearly with increasing temperature in nearly the same manner for both metals. Generally the work of adhesion of the metals to the oxides increased as the temperature increased. As a result of this the contact angles decreased with increasing temperature.

Of the materials studied, beryllia was found to be the best refractory for containing the molten metals. The reactions between the metals and beryllia were less extensive than the other refractories, and the metal did not diffuse into the beryllia plaques. Zirconia was found to be a possible container for the molten metals, though the metal did penetrate the refractory by diffusion. Thorium and alumina were found to be poor container materials for the metals.

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#### ANTHRACNOSE OF KENAF CAUSED BY *COLLETOTRICHUM HIBISCI* POLL.<sup>1</sup>

Herbert G. Pulsifer<sup>2</sup>

Department of Botany

*Colletotrichum hibisci* Poll., the causal organism of anthracnose of kenaf (*Hibiscus cannabinus* L.) was isolated repeatedly from plants in a plot of kenaf at Ames, Iowa, during the summer of 1952. Incomplete information in the phytopathological literature on symptoms and symptomology, the causal organism, the disease cycle, and the possible hosts, made a study of these phenomena the primary objective of this investigation.

The most obvious symptoms in the field are death of the apical portion of the plant and typical anthracnose lesions on the stem. Repeated observations of kenaf in the field, however, indicated that under certain climatic conditions, these more obvious symptoms become masked with continued growth and are succeeded by a characteristic stunting and malformation.

A positive confirmation of the hypothesis that *Colletotrichum hibisci* is seed-borne on kenaf seed was obtained in greenhouse experiments where

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<sup>1</sup>Doctoral thesis number 1724, submitted October 13, 1955.

Chairman of Committee, W. F. Buchholtz, Department of Botany.

<sup>2</sup>B.A., University of Maine, Orono. M.S., *ibid.* Graduate Assistant.

kenaf seed was planted in steamed soil along with suitable checks. Kenaf seed harvested from kenaf plants previously infected by C. hibisci was shown to harbor sufficient inoculum of this fungus to induce up to 100 per cent damping-off of the resulting seedlings, when planted in sterilized greenhouse soil. Likewise, seeds infested by means of a conidial suspension of C. hibisci produced up to 100 per cent of damped-off seedlings. In an experiment where seed harvested from kenaf plants previously infected by C. hibisci in the field was used along with seed infested by means of a spore suspension, C. hibisci was isolated in pure culture from 39 of 113 damped-off seedlings.

Incidental to the above study, it was discovered that within a mixed population of 3657 purple, red, and green kenaf plants growing at Ames under conditions of natural infection in the field, none of the purple kenaf (Hibiscus cannabinus var. purpureus) exhibited any stem lesions or tip blight, while 22.5 per cent of the red kenaf (H. cannabinus var. ruber) and 35.8 per cent of the green kenaf (H. cannabinus var. vulgaris) showed tip blight or stem lesions, or both.

Similarly, in the greenhouse, 60 per cent of the plants of the variety purpureus remained undamaged after application of a conidial suspension of C. hibisci, as against only 20 per cent of the variety vulgaris; however, there was little or no difference in susceptibility between the purple and the green varieties when wounding was employed in the technique of inoculation.

Another topic of investigation involved a study of the pathogenicity of C. hibisci to hosts other than kenaf, in conjunction with a comparative study of C. hibisci and C. gossypii South. (Glomerella gossypii (South.) Edgerton).

Of significance during the study of additional hosts of Colletotrichum hibisci was the successful recovery of this fungus from 33 of 62 seeds of okra (Hibiscus esculentus L.) which had remained in infected capsules in the field during the winter. These capsules had been infected by hypodermic injection the previous summer, and the fact that the inoculum of C. hibisci within the seeds was still viable after passing the winter in the field indicated that this fungus might live over the winter in the field under the climatic conditions which prevail in Iowa.

Isolates of C. hibisci obtained from kenaf plants infected at Ames, and isolates from kenaf seed infected in Florida, were capable of infecting both mature and seedling plants of three varieties of okra, as well as the seedling plants of a variety of Upland cotton, La 33. Damping-off of the cotton seedlings caused by the isolates of C. hibisci was severe, and the symptoms were indistinguishable from those caused by C. gossypii South. Damage to cotton seedlings infected with C. hibisci, after emergence following spray application of a conidial suspension, was not severe, being limited to a spotting of the two or three youngest leaves.

Four successive attempts at infestation of the seed failed to induce infection of kenaf seedlings by C. gossypii. It seemed evident that the isolates of C. gossypii used in these experiments did not possess the virulence for kenaf seedlings possessed by the isolates of C. hibisci. Notwithstanding these failures to induce infection of seedling kenaf plants, C. gossypii did infect young kenaf plants after a series of passages of the inoculum through the kenaf host. At the end of four successive passages through kenaf, the two isolates of C. gossypii produced symptoms indistinguishable from those produced by C. hibisci.

During the inoculation trials with C. hibisci and C. gossypii, the identity of the two species was checked after isolation by observing and measuring the lengths of the conidia and colony growth at 25, 32, and 37°C. When grown on comparable media for five days, the conidia of C. hibisci were, on the average, 10-11 microns long, in contrast to a length of 14-15 microns for conidia of C. gossypii.

When cultured at 13, 18, 25, 32, and 37°C, optimum growth of both C. hibisci and C. gossypii occurred at 25°C, with C. gossypii growing notably



faster at this temperature. There was limited growth of *C. hibisci* at 32°C, at which temperature *C. gossypii* grew nearly as well as at 25°C. *C. hibisci* did not grow at all at 37°C, while *C. gossypii* continued to make some growth at this temperature. In all cases these differences in growth were conspicuous and consistent, and seemed a reliable criterion for the separation of the two species.

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### PATHOLOGY AND CLINICAL FINDINGS OF SO-CALLED MUCOSAL DISEASE OF CATTLE<sup>1</sup>

Frank K. Ramsey<sup>2</sup>

Department of Veterinary Pathology

In 1951 an apparently new disease in cattle was encountered and named mucosal disease. Since that time, cattle with this condition from 12 affected herds in 1951, 12 herds in 1952, 17 herds in 1953, 23 herds in 1954, and 25 herds in 1955 have been admitted to the Iowa State College Veterinary Clinic for study and diagnosis. A diagnosis of mucosal disease has been made in animals necropsied at the Iowa Veterinary Medical Diagnostic Laboratory from 22 additional herds. Mucosal disease has now been recognized in 20 states and in Canada.

This condition has been seen predominantly in Hereford and Aberdeen Angus cattle, and it has been found in Shorthorn, Holstein-Friesian, and Guernsey breeds. Most of the animals have been between six and 14 months of age. The incidence has been greatest in winter and early spring, especially in the months of February and March, but it has occurred in every month of the year. The morbidity rate varied from two to 50 per cent in different herds, and the mortality rate of affected animals was above 90 per cent.

Mucosal disease is characterized by initial elevation of temperature, with lysis in two or three days, decreased appetite followed by anorexia, constant or intermittent severe diarrhea often hemorrhagic, rapid dehydration and marked loss of weight. Slight opacity of one or both corneas and increased lacrimation were noted in ten herds. There were no central nervous symptoms. Examination of the nostrils, muzzle, lips, gums, tongue, and oral cavity usually revealed erosions and ulcerations of varying sizes and shapes. Foul-smelling mucopurulent exudate was often observed hanging from the nostrils and muzzle.

Routine bacteriologic culture studies of kidneys, liver, spleen, and heart blood gave uniformly negative results. Transmission studies were inconclusive.

Blood studies revealed an undulation of leucocyte numbers with transient leucopenia.

Complete necropsy examinations were performed on 116 animals from 87 herds. Microscopic studies represent approximately 5000 tissue sections taken from 103 animals.

Pathologic alterations in this disease varied considerably. The lesions were primarily erosive, ulcerative, and cystic; being confined principally to

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<sup>1</sup>Doctoral thesis number 1753, submitted December 9, 1955. Chairman of Committee, E. A. Benbrook, Department of Veterinary Pathology.

<sup>2</sup>B.S., Northern State Teachers College, Aberdeen, South Dakota.

D.V.M., Iowa State College, Ames.

Assistant Professor, Veterinary Medicine Research Institute.

the lamina epithelia and mucosa of the alimentary canal. Hyperemia and hemorrhage were common findings, but marked leucocytic infiltrations expected to accompany severe gross lesions were not always found.

The liver generally appeared normal, but cloudy swelling, fatty degeneration, and centrolobular necrosis were observed in some cases. Usually no macroscopic or microscopic lesions of the pancreas were found. No lesions were found in the serous salivary glands, but an excessive production of mucus was always found in the mucous salivary glands.

Lesions of the circulatory system consisted of hyperemia, hemorrhages, thromboses, arteritis, and periarteritis. Lymph nodes often showed no manifest reaction or were only slightly edematous. Micropathologic alterations were definite in many lymph nodes. The lesions showed a marked decrease in the mononuclear cells and in coagulation necrosis of the lymph nodules.

Erosions extended from the muzzle into the nares for 3 or 4 cm in about 80 per cent of the cattle. Catarrhal rhinitis with erosions and ulcerations of the anterior ventral turbinate was present in many animals.

Macroscopic lesions of the kidneys were not usually evident, but medullary hyperemia and fatty degeneration were sometimes observed on gross examination. The most consistent microscopic alteration was pronounced cloudy swelling of renal epithelium. Catarrhal, severe erosive, and ulcerative posthitis were frequently found. Necrotic vulvitis of the labis was found in some females.

Gross microscopic alterations of the central nervous system were not found except for some passive hyperemia and edema.

In most instances gross thickening of the skin could not be palpated, but histologic examination did sometimes reveal a focal proliferative dermatitis.

History, symptoms, laboratory findings, gross and microscopic lesions should enable one to differentiate mucosal disease from virus diarrhea (New York), virus diarrhea (Indiana), epizootic enteritis in cattle (Sweden), bovine malignant catarrh, bovine hyperkeratosis (X-disease), and other diseases.

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#### ESTIMATION OF LIMITING CHARACTER OF THE HYDROLYSIS REACTION OF BENZYL TOSYLATES<sup>1</sup>

Charles E. Reeder<sup>2</sup>

Department of Chemistry

The rates of hydrolysis of a series of substituted benzyl tosylates (p-toluenesulfonates) have been determined in a series of aqueous organic solvent mixtures of low dielectric and of varying composition. The  $pK$  values of the first order rate constants for the compounds, solvents, and temperatures employed are given in Tables 1 and 2.

The  $pK$  values of these reactions give linear modified Hammett  $\rho\sigma$  plots with a value of  $-\sigma^*$  larger than the usual Hammett value for those compounds whose substituent group can enter into resonance with the developing positive charge on the benzyl carbon due to heterolytic cleavage of the C-O bond. However, within a given solvent type the value of  $\sigma^*$  is constant. Since  $-\sigma^*$  increases with increased possibility for resonance by the substituent, such a

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<sup>1</sup>Doctoral thesis number 1719, submitted September 12, 1955.

Chairman of Committee, George S. Hammond, Department of Chemistry.

<sup>2</sup>B.S., Wheaton College, Wheaton, Illinois.

Graduate Assistant, Industrial Science Research Institute.

constant value of  $\sigma^*$  indicates that the amount of ionic character of the old bond does not change noticeably as one increases the electrophilic character or ionizing power of the solvent by addition of water. Since the ionic character of the bond does not increase with these solvent properties, the bond must be nearly completely ionized in all cases, and therefore the solvolysis of benzyl tosylates is truly a limiting reaction, contrary to the conclusions of most previous solvolysis correlations. A slightly larger value of  $-\sigma^*$  is obtained in acetone systems than in those of dioxane; the former, being poor nucleophilic solvating agents, therefore require a greater amount of internal stabilization of the ion formed

Table 1.  $p_k$  Values for hydrolysis of benzyl tosylates in aqueous acetone

Subst. <sup>a</sup>	Temp. °C	Solvent composition <sup>b</sup>		
		83.3%	90.9%	96.2%
H	25	5.05	5.61	6.39
	35	4.59	5.15	---
	45	4.11	4.69	5.48
NO <sub>2</sub>	25	6.30	6.76	7.45
	45	5.38	5.83	6.58
Cl	25	5.22	5.76	6.50
	35	4.74	5.26	---
	45	4.32	4.86	5.56
F	25	4.74	5.37	6.13
	45	3.83	4.50	5.23
Me	25	3.72	4.46	5.26
	35	3.22	3.98	---
	45	2.77	3.52	4.35
C <sub>6</sub> H <sub>5</sub>	25	4.12		
	45	3.10		
m-C <sub>6</sub> H <sub>5</sub>	25	5.21		
	45	4.30		

<sup>a</sup>Substituents in para position except m-C<sub>6</sub>H<sub>5</sub>.

<sup>b</sup>Volume per cent for ideal solution at 25°.

The  $\rho$  values present an anomaly in that they vary in the opposite direction from  $\sigma^*$  as one goes from acetone to dioxane systems. However,  $\rho$  increases with water concentration for all solvent mixtures.

The amount of the increase in  $-\sigma^*$ ,  $\Delta\sigma$ , for m- and p-phenyl substituents correlate quantitatively with additional delocalization energies of the two biphenylmethyl carbonium ions obtained by simplified molecular orbital calculations. This gives additional evidence that  $\Delta\sigma$  is a measure of increased resonance effects. A much larger value of  $\Delta\sigma$  for the p-fluoro substituent than for p-chloro supports the postulate that the outer orbital, nonbonding electrons of fluorine have a greater ability to enter into resonance with an unsaturated system than do those of chlorine even though the former is more electronegative.

Table 2.  $pK$  Values for hydrolysis of benzyl tosylates in aqueous dioxane

Subst. <sup>a</sup>	Temp. °C	Solvent composition <sup>b</sup>		
		55.6%	66.7%	76.9%
H	25	3.40	3.95	4.43
	35	2.97	3.49	3.98
	45	2.53	3.07	3.53
NO <sub>2</sub>	25	5.32	5.62	5.98
	35	4.79	5.13	---
	45	4.35	4.71	5.10
Cl	25	3.67	4.24	---
	35	3.24	3.77	---
	45	2.82	3.33	---
F	25	2.96	3.60	4.15
	45	2.17	---	3.24
Me	25	1.76	2.45	3.12
	35	1.35	2.05	2.69
	45	---	---	2.22
C <sub>6</sub> H <sub>5</sub>	25	2.29	2.98	---
m-C <sub>6</sub> H <sub>5</sub>	25	3.72	4.22	---

<sup>a</sup>Substituents in para position except m-C<sub>6</sub>H<sub>5</sub>.<sup>b</sup>Volume per cent for ideal solution at 25°.

The values of  $-\Delta S^*$  for benzyl tosylate hydrolysis decrease with increase in water concentration as does the  $-S$  of ionization of acids in similar media, indicating a greater amount of orientation is required for a poorer solvating agent. A reversal of the above order was noted, however, for the p-fluoro and p-chloro compounds. The value of  $-\Delta S^*$  also decreases qualitatively with the amount of delocalization of the charge on the benzyl ion expected due to resonance with the substituent,  $-\Delta S^*$  being least for the very large p-phenylbenzylcarbonium ion.

The following properties of p-fluoro- and m-phenylbenzyl alcohols, which have not apparently been previously isolated in pure form, are reported: for

p-fluorobenzyl alcohol, M.P., 22-23°; B.P., 209°;  $n_D^{20}$ , 1.5080; for m-phenylbenzyl alcohol (m-biphenyl carbinol), M.P., 51.2-51.5°.

IODATO-SILVER COMPLEXING EQUILIBRIA<sup>1</sup>James J. Renier<sup>2</sup>

Department of Chemistry

Solubilities of silver iodate in aqueous solutions containing various concentrations of lithium iodate have been measured for 25.0°C, 35.0°C, and 50.5°C by means of an improved radioassay technique for silver activity. They have also been measured for the same temperatures in aqueous solutions containing various proportions of lithium iodate and lithium perchlorate. In the latter experiments, the ionic strengths of all equilibrium solutions were fixed at a value of 1.00 M.

The refined radiotracer method was based upon an electrodeposition procedure for mounting samples for counting. Samples of the equilibrium solution phases from the equilibrated mixtures were carefully added to portions of strong nitric acid solutions which contained a predetermined amount of silver carrier (usually 10 mg). To insure complete exchange between the tracers and the carriers, the solutions were evaporated to dryness. The residues were subsequently dissolved in ammoniacal cyanide plating baths and a current of 0.2 amp was passed through the resulting solutions for a period of thirty-five minutes. The silver that was uniformly deposited was determined gravimetrically and was counted to determine its activity. From these data the activities corresponding to 100 per cent recovery of the carriers were computed. The application of corrections for self-absorption and radioactive decay converted the observed activities to ones which were proportional to the tracer concentrations in the various aliquots of the equilibrium solution phases. A knowledge of the specific activity of the silver used in the experiments made the radioassay complete.

A series of experiments performed to test the procedure for sampling of equilibrated mixtures have been discussed at some length. The results have indicated that an evaluation of the method used to obtain equilibrium solution samples should form an integral part of all solubility measurements in which radiotracers are employed.

The solubility data have been interpreted in terms of chemical equilibria which involve the species  $\text{Ag}^+$ ,  $\text{AgIO}_3(\text{aq.})$ , and  $\text{Ag}(\text{IO}_3)_2^-$ . Equilibrium solubility product constants for  $\text{AgIO}_3(\text{s})$  in aqueous solution were obtained from the results of measurements performed in solutions for which ionic strengths were low and variable. The values of these quantities for 25.0°C, 35.0°C, and 50.0°C were observed to be  $(3.0 \pm 0.15) \times 10^{-8}$ ,  $(6.3 \pm 0.3) \times 10^{-8}$  and  $(17.4 \pm 1.0) \times 10^{-7}$ , respectively. Equilibrium formation constants for the monoiodatosilver and the diiodatosilver complexes were estimated from the measurements performed for solutions of constant ionic strength. At 25.0°C, 35.0°C, and 50.0°C the values determined for the monoiodatosilver species were  $4.26 \pm 2.62$ ,  $6.34 \pm 1.86$ , and  $9.09 \pm 1.16$ , respectively, while those for the diiodatosilver species were  $79.4 \pm 5.2$ ,  $66.4 \pm 4.3$ , and  $41.1 \pm 3.0$ , respectively. It was observed that representations of the experimental data obtained for low, variable ionic strengths were adequately reproduced by means of suitable equations and the equilibrium formation constants obtained for constant ionic strength.

From the solubilities and their temperature coefficients thermodynamic quantities for the iodato complexes have also been computed. The entropy change calculated for the reaction to form  $\text{AgIO}_3(\text{aq.})$  was  $20.3 \pm 14.7$  e.u.

<sup>1</sup>Doctoral thesis number 1694, submitted July 8, 1955.

Chairman of Committee, Don S. Martin, Department of Chemistry.

<sup>2</sup>B.S., College of St. Thomas, St. Paul, Minnesota.

Research Assistant, Institute for Atomic Research.



and that calculated for the reaction to form  $\text{AgUO}_2)_2^-$  was  $-8.50 + 2.55$  e.u. These values were found to be in fair agreement with a semi-empirical formulation.

The thermodynamic description of the silver iodate-iodate ion-water system that was obtained was not definitive in an absolute sense in that iodate ion appeared to be a very weak complexing agent for silver and the monoiodatosilver species possessed a low stability which was difficult to evaluate quantitatively.

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## PLEISTOCENE GEOLOGY AND SOILS IN SOUTHERN IOWA<sup>1</sup>

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Departments of Geology and of Agronomy

Because of the shortage of sand and gravel in southern Iowa, it is desired to know about the nature and properties of Pleistocene sediments so that they can be stabilized most efficiently for use in engineering structures. The study was restricted largely to the till, loess, and gumbotil. Petrography and clay mineralogy were emphasized, but sedimentation, stratigraphy, weathering, diagenesis, geomorphology, and soil genesis were also of some interest.

The procedures used included mechanical analysis, differential thermal analysis, X-ray spectroscopy, petrographic analysis of  $5\mu$  to 2 mm material, field observation, and topographic profiles.

The till and loess have a similar particle size range below  $5\mu$ , but above  $5\mu$  they have a distinctive particle size distribution. The gumbotils seem to be developed from either till or loess.

The clay mineralogy of the till, gumbotil, loess, and soil horizons is the same throughout the area. An illite-montmorillonite mixed-layer clay dominates. Illite, Kaolinite, and quartz are also present in the clay fraction.

In the material coarser than  $5\mu$ , quartz and feldspar dominate in all horizons of the till and loess. The heavy mineral suite of till and loess are similar, but the proportions indicate that the till is more weathered than the loess.

Field observations and topographic profiles suggest that pedimentation, which consists essentially of parallel slope retreat, is at the dominant process of landscape evolution. Slope retreat in this area is primarily due to slumping and creep, but sheet wash and gully gravure are important locally. The broad flats in the area are remnants of former pediments.

It is suggested that only one drift sheet, called Kansan, be recognized until modern stratigraphic concepts and tools can be applied. The thickness of the upland loess is independent of divide elevations and therefore the loess is considered to be an aeolian deposit which is younger than the pediment remnants.

The till and loess tend to creep toward the valleys as dissection by streams progresses. Many minor features of the till and loess are interpreted as the result of mass movement, local intense diagenesis related to this mass movement and diagenesis alone.

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<sup>1</sup>Doctoral thesis number 1791, submitted May 24, 1956.

Chairmen of Committee, Chalmer J. Roy, Department of Geology, and F.F. Riecken, Department of Agronomy.

<sup>2</sup>B.S., Michigan State University, East Lansing. M.S., *ibid*.

Instructor, Geology. Associate, Engineering Experiment Station.

Diagenesis consists primarily of the formation of carbonate concretions, iron oxide concretions, and manganese oxide concretions. The depth of carbonate accumulation represents an equilibrium between ground water deposition and downward leaching by surface waters. These are controlled by landscape evolution. Therefore depth of leaching is not a valid measure of the age of the drift.

Weathering under the climate of this region is primarily a splitting process resulting from the growth of alteration products within the mineral grain. Weathering tends to be more intense near the soil surface.

Using recognized principles of weathering and sedimentation, it is demonstrated that the regional trends in clay content in the loess and loess-derived soils cannot be due to sedimentation. It is recognized that some clay is the product of sedimentation and some is the product of weathering.

The soil associations are indirectly related to landscape evolution. It is concluded that the same basic techniques of soil stabilization will apply to the till, gumbotil, loess, and probably alluvial deposits of the area.

Because of alluviation by Pleistocene streams, geophysical prospecting for sand and gravel will be most successful in the uplands adjacent to modern valleys. It will also be successful in areas of thin loess although the gravels and sands will have a high content of impurities.

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## AMINE OXIDES AS OXIDIZING AGENTS<sup>1</sup>

Robert John Rolih<sup>2</sup>

Department of Chemistry

The oxidation of organic compounds containing active halogen atoms by the action of amine oxides may be considered to take place in two discrete steps. The first step is a displacement by the amine oxide of halogen with the formation of an amine oxide salt and the second is the disproportionation of the salt so that a carbonyl group occupies the position formerly held by the halogen. Under suitable conditions, the two steps may occur as one.

The value of using amine oxides as oxidizing agents in intermolecular reactions has not been investigated to any great extent. Thus, the process was studied in the hope of determining its feasibility as a synthetic route to carbonyl compounds.

The amine oxides of trimethylamine, quinuclidine, pyridine, and benzonitrile were selected for steric and electronic reasons as representative oxidizing agents. For similar reasons, *p*-nitrobenzyl bromide,  $\alpha$ -chlorocyclohexanone, 4-bromocoprostanone, cyclohexyl bromide, and cholesteryl chloride were chosen as substrate molecules.

In the oxidation of *p*-nitrobenzyl bromide to *p*-nitrobenzaldehyde, quinuclidine oxide was found to be the most effective oxidizing agent followed by trimethylamine, pyridine, and benzonitrile oxides. Benzonitrile oxide followed by trimethylamine oxide were the best oxidizing agents for the conversion of  $\alpha$ -chlorocyclohexanone to cyclohexane 1,2-dione. Quinuclidine and pyridine oxides were the least reactive. A side product, cyclohexenone was formed by an elimination reaction which occurred during each of the oxidations.

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<sup>1</sup>Doctoral thesis number 1779, submitted March 13, 1956.

Chairman of Committee, Ernest Wenkert, Department of Chemistry.

<sup>2</sup>B.S., University of Illinois, Urbana.

Graduate Assistant, Industrial Science Research Institute.

An unidentified  $\alpha$ -diketone was obtained from the oxidation of 4-bromocoprostanone instead of the known 4-hydroxycholestenone. Elimination again took place with the formation of cholestenone.

Neither cyclohexyl bromide nor cholesteryl chloride was capable of being oxidized by the amine oxides used. However, elimination of hydrogen bromide from cyclohexyl bromide took place instead.

Attempts to use trimethylamine oxide under acidic conditions as an electrophilic oxidizing agent on compounds such as benzene, cyclohexene, phenanthrene and hydroquinone were unsuccessful.

A new synthesis of quinuclidine has been reported. Phenyl lithium in an exchange reaction with  $\gamma$ -picoline yielded  $\gamma$ -picolyl lithium which, after carbonation and esterification, yielded ethyl 4-pyridineacetate. Catalytic reduction of the heterocyclic ring followed by lithium aluminum hydride reduction of the ester group resulted in 4-piperidineethanol. This was then converted to quinuclidine by conventional methods.

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#### DIFFUSION, SORPTION AND DEPTH DISTRIBUTION OF OXYGEN IN SOILS<sup>1</sup>

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Department of Agronomy

It is generally accepted that the space and composition of the soil atmosphere influence plant growth. Because of the accepted importance of aeration, essentially all of the physical properties of soil are interpreted in terms of their influence on soil aeration. In spite of the generally accepted relationship between the physical properties of soil and soil aeration there are few quantitative data on the subject.

In 1952 synthetic organic materials were introduced which exhibited remarkable powers of stabilizing soil aggregates. This material offered the opportunity of studying the effect of stability of soil aggregates on the oxygen concentration of the soil, on other physical observations and also on crop response. The organic materials were applied to the surface 6 inches of two soils, the Webster silty clay loam and the Edina silt loam. As measured by aggregate analysis, the aggregate stability of both soils was greatly improved by the application of the synthetic organic material. Improving the stability of the surface 6 inches of either soil had no measurable effect on the oxygen concentration of the soil atmosphere in the treated zone or at greater depths. The oxygen concentration of the soil atmosphere at the different depths did, however, follow an interesting pattern. In the early part of the 1953 growing season, oxygen concentration of the soil atmosphere at the different depths decreased in the order 3 inches, 1 foot, 3 feet, and 2 feet. Toward the end of the growing season, the order of decreasing oxygen concentrations was 3 inches, 1 foot, 3 feet, and 2 feet. In general, the order of magnitude of the oxygen concentration of the soil atmosphere at all depths was low at the beginning of the growing season when the moisture content was high. Likewise, at the end of the growing season when the moisture content was low the oxygen concentration of the soil atmosphere was high.

<sup>1</sup>Doctoral thesis number 1788, submitted May 21, 1956.

Chairman of Committee, Don Kirkham, Department of Agronomy.

<sup>2</sup>B.S., Agricultural and Mechanical College of Texas, Bryan. M.S., *ibid.* Associate, Agricultural Experiment Station.

Stabilizing the aggregates in the surface 6 inches of the Webster silty clay loam soil had no effect on the moisture content of the soil in either the treated zone or at greater depths. In the spring, the moisture content of the Edina silt loam soil was higher in the synthetically stabilized soil than in the unstabilized soil. By early summer the moisture content of the stabilized soil was lower than that of the unstabilized soil. Stabilizing the aggregates on the surface 6 inches of the Edina silt loam had no effect on the moisture content of the soil other than in the treated zone.

The potassium content of the corn leaves was not influenced by stabilizing the surface aggregates on the Webster silty clay loam. There was a trend for the potassium content of the corn leaves to be increased by application of the conditioner to the Edina silt loam. Corn yields on the Webster silty clay loam were not influenced by stabilizing the surface aggregates. On the other hand, an increase of about 10 bu/acre resulted from stabilizing the surface aggregates of the Edina silt loam.

Diffusion is generally considered to be the major process by which oxygen is supplied to plant roots and carbon dioxide removed from plant roots. It has been found by experimentation that the diffusion rate in soils is related to the fraction of pore space in soil occupied by air. It has also been found that the evolution of carbon dioxide by the soil microorganisms influences the determination of the diffusion constant of carbon dioxide. At the present time, considerable emphasis is being placed on the determination of the diffusion constant of oxygen for soils. A study was made to determine the extent which consumption of oxygen in soil influences the total diffusion of oxygen and on the diffusion constant itself. Phenol solution was used to prevent microbial consumption of oxygen and sucrose solution was used to stimulate microbial consumption. The phenol solution was found to be effective in preventing microbial consumption.

Diffusion was studied in 1 1/2-inch cores of soil prepared in the laboratory at 10, 50, 100, 300 cm of water, and 1 atm. tension. It was found that as the tension of water increased, diffusion of oxygen increased. This was a result of increasing the volume of air filled pores in the cores as the tension increased. At the low tensions of water (high moisture content), the quantity of oxygen diffusing through the soil cores was decreased by the consumption of oxygen in the soil cores. The consumption of oxygen by the soil microorganisms would thus decrease the value of the measured diffusion constant of the soil for oxygen. At high tensions of water, the consumption of oxygen by the soil microorganisms had little influence on the total quantity of oxygen diffusing through the soil.

An aspect of soil aeration which has received essentially no attention is the quantitative evaluation of oxygen in the liquid phase of soils. It has been known for some time that oxygen is adsorbed by dry soil particles and that oxygen is dissolved in aqueous solutions. It was desired to know if water adsorbed by the soil particles influences the adsorption of oxygen and if the soil solution will dissolve oxygen as readily as does free water. Sorption of oxygen at 25°C was measured on air-dry and oven-dry Webster silty clay loam, Ida silt loam, Edina silt loam, Edina subsoil and quartz sand as well as vermiculite and Edina subsoil moistened to different moisture contents. The results of the sorption of oxygen by air-dry and oven-dry soils indicate that the adsorption of water, as in the case for air-dry soils, decreases the adsorption of oxygen. The adsorption of oxygen by oven-dry soils was found to be related to the clay content of the soil. On the vermiculite-water system, between the moisture contents 75 per cent to 300 per cent, a linear relationship was obtained for sorption of oxygen and the moisture content of the vermiculite. The amounts sorbed were equivalent to that which would dissolve in free water. In the moisture range 0 to 75 per cent, the sorption of oxygen by the vermiculite-water system was in excess of that which would dissolve in the water itself. In the sorption of oxygen by the Edina subsoil-

water system, it was found that at about 28 per cent moisture the amount of oxygen sorbed was equivalent to that of free water. In the moisture range 14 to 28 per cent there appeared to be a reduction in the amount of oxygen sorbed as compared to free water. At moisture contents below 12 per cent there was a greater quantity of oxygen sorbed than could be accounted for by solubility in water alone.

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CYTOLOGICAL STUDIES OF HYBRIDS INVOLVING  
TRITICUM DURUM AND SECALE CEREALE<sup>1</sup>

Kiyoshi Sadanaga<sup>2</sup>

Department of Genetics

Hybrids were secured from crosses between Triticale, the allopolyploid of *Triticum durum* var. Carleton and *Secale cereale*, and the durum varieties Lumillo, F.P.I. 94587 and Stewart, and spring rye. Crosses of Triticale to the durum variety Golden and to selfed Dakold, a winter rye, were unsuccessful. The hybrids between Triticale and the durum varieties F.P.I. 94587 and Stewart had pubescent peduncle (hairy neck) conditioned by genes or gene on chromosome I of rye. At MI, PMCs with  $14\text{II} + 7\text{I}$  were observed most frequently. Nonhairy neck hybrids with 31 and 32 somatic chromosomes were derived from a cross between Triticale and Lumillo. The number of bivalents in the PMCs ranged from 11 to 14 with the mode at 14 bivalents. The high frequency of cells with 14 bivalents indicated that these hybrids originated from the fertilization of a Triticale egg of ABS-3 or ABS-4 constitution by a gamete of the AB constitution of tetraploid wheat. Quadrivalents usually in the form of a ring of four chromosomes were observed in all hybrids involving durum varieties. The frequency of microsporocytes with quadrivalents in the hybrids involving Lumillo ranged from 19.0 to 37.1 per cent. The segregation into ring forming and normal plants of the backcross and self progenies of the hybrids, as well as the absence of quadrivalents in the hybrids between Triticale and rye, indicated that the ring of four chromosomes is probably due to a reciprocal translocation between wheat chromosomes, the interchange originating in Triticale.

Two hybrids with and four without the hairy neck character were secured from a cross between Triticale and spring rye. Cells with 5 bivalents were observed most frequently at MI in the four nonhairy neck plants which had 25 and 26 somatic chromosomes. The hairy neck plants which were phenotypically similar had 27 somatic chromosomes. Cells with 3 bivalents in one of the plants and 6 in the other were observed most frequently. Approximately 38 per cent of the PMCs in the latter plant had trivalents.

A 29 chromosome plant monosomic for chromosome I of rye was derived from a backcross of the hybrid between Triticale and F.P.I. 94587 to Khapli. The presence of the rye chromosome adversely affected plant height and increased the frequency of asynapsis of one or two pairs of wheat chromosomes.

Approximately 83 per cent of the self and backcross progenies of the hybrids involving durum varieties had 28 or 29 somatic chromosomes. This indicated that gametes with the AB genomes of tetraploid wheat and gametes with the AB genomes plus 1 rye chromosome were more effective in fertilization than gametes with AB plus 2 or more rye chromosomes.

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<sup>1</sup>Doctoral thesis number 1726, submitted October 17, 1955.

Chairman of Committee, J. G. O'Mara, Department of Genetics.

<sup>2</sup>B.S., University of Hawaii, Honolulu. M.S., Iowa State College, Ames.



MASS SPECTROMETRIC STUDY OF METALLIC COHESIVE ENERGIES<sup>1</sup>William Ralph Savage<sup>2</sup>

Department of Physics

A sensitive method was used for measuring rapidly the latent heat of vaporization or sublimation of metals of moderate volatility. A modification of the effusion method of determining vapor pressure was employed to obtain the values reported. Atoms from a saturated vapor effuse from a Knudsen-type vapor cell and impinge upon a heated ribbon. A fraction re-evaporate as positive ions and are observed with a mass spectrometer of conventional design. The Clausius-Clapeyron equation is used to obtain the latent heat of vaporization from the dependence of ion current upon the cell temperature. Only a slight degree of surface ionization at the ribbon is required for the measurement of latent heats.

An application of the method has been made to aluminum, dysprosium, samarium, thulium, and ytterbium. The work on aluminum redemonstrated the utility of the procedure and yielded an enthalpy of vaporization of  $73.5 \pm 0.4$  kilocalories per mole vaporization at  $1327^\circ\text{K}$ . Values were obtained for the change in enthalpy per mole for sublimation of certain rare earths. They are: dysprosium,  $69.3 \pm 0.6$  kcal for vaporization at  $1215^\circ\text{K}$ ; samarium  $48.7 \pm 0.4$  kcal for vaporization at  $811^\circ\text{K}$ ; thulium,  $56.2 \pm 0.4$  kcal for vaporization at  $937^\circ\text{K}$  and ytterbium,  $39.5 \pm 0.5$  kcal for vaporization at  $667^\circ\text{K}$ . The mass spectrometric method provides a convenient way to measure first-order phase transitions.

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<sup>1</sup>Doctoral thesis number 1805, submitted June 1, 1956.

Chairmen of Committee, F. H. Spedding, Department of Chemistry, and D. E. Hudson, Department of Physics.

<sup>2</sup>B.S., Iowa State College, Ames.

Graduate Assistant, Institute for Atomic Research.

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REPRESENTATION OF POWER SYSTEM LOADS  
FOR FAULT STUDIES<sup>1</sup>G. Dale Sheckels<sup>2</sup>

Department of Electrical Engineering

This paper presents a method of representing power system loads by adjusted constant impedances. The method retains all the convenience of earlier constant impedance methods, but gives a more accurate representation during and shortly after the fault. The loads are divided into the three important types--induction motors, synchronous motors, and lighting and heating loads--and each type is discussed separately.

The simple hypothetical power system used for these studies consists of a double-circuit transmission line connected at its sending end to an infinite bus and at its receiving end to a synchronous motor in parallel with the load being

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<sup>1</sup>Doctoral thesis number 1706, submitted August 5, 1955.

Chairman of Committee, W. B. Boast, Department of Electrical Engineering.

<sup>2</sup>B.S., University of Washington, Seattle. M.S., Massachusetts Institute of Technology, Cambridge.

considered. A three-phase fault is placed on one circuit of the transmission line at its midpoint and is cleared 0.2 second later by simultaneous opening of circuit breakers at the two ends of the faulted circuit. The effect of the load on the swing curve of the synchronous motor is then studied.

When the load consists of a large number of small induction motors, it is simulated by a single equivalent induction motor having per unit parameters equal to the averages of the small motors. The entire system equivalent circuit is set up on the network analyzer in such a manner that the induction motor torque may be measured directly. This measured value of torque together with the assumed value of induction motor inertia is used to find the deceleration of change in slip during each succeeding time interval in the step-by-step calculations. The slip at the end of the time interval is then used to find the new induction motor parameters at the beginning of the next time interval. These step-by-step calculations give the exact swing curve for the synchronous motor which is the basis for comparison of the approximate methods. The equivalent induction motor parameters are then held constant at values corresponding to several increased levels of pre-fault loading and the step-by-step calculations are repeated. The impedance corresponding to the pre-fault loading which gives a swing curve most nearly approximating the exact curve is the constant value which may be used throughout the transient interval. Six combinations of inertia and rating are assumed for the induction motor, the inertias being 100, 25, and 6.25 per cent of the synchronous motor rating.

When the load consists of a large number of synchronous motors, it is simulated by a single equivalent synchronous motor, designated as motor no. 3, in parallel with the original synchronous motor, no. 2, which was used for the induction motor studies. Nine combinations of power factor and inertia are assumed for motor no. 3, the power factors being unity, 0.8 lagging, and 0.8 leading, and inertias being 400 per cent, 100 per cent, and 25 per cent of the inertia of motor no. 2. Motor no. 3 has a rating equal to 25 per cent of that of no. 2. The exact swing curves for motor no. 2 are found by the conventional three-machine step-by-step procedure and the approximate curves, with a fixed impedance substituted for no. 3, by the two-machine procedure.

Studies are also made in a similar manner on lighting loads consisting of incandescent lamps, slimline fluorescent lamps and starter-type fluorescent lamps.

The following conclusions are drawn from these studies:

1. When an equivalent induction motor load has an inertia constant equal to that of an adjacent synchronous motor, the induction motor may be represented by its constant pre-fault impedance throughout the transient interval.
2. If the induction motor has an inertia constant one-fourth that of the synchronous motor, it may be represented by an impedance corresponding to a 100 per cent increase in its pre-fault load torque.
3. For an inertia constant ratio of one to sixteen, the necessary load torque increase is about 230 per cent.
4. The above three conclusions are valid for cases where the equivalent induction motor rating is equal to the synchronous motor rating and for cases where it is one-fourth of the synchronous motor rating.
5. When an equivalent synchronous motor has a rating of one-quarter that of a second adjacent synchronous motor and when their inertia constants are equal, the equivalent machine may be replaced during the transient period by a fixed resistance equal to 20 per cent of its pre-fault equivalent

resistance. This is valid when the pre-fault power factor of the equivalent machine is unity, 0.8 lag, or 0.8 lead.

6. When the equivalent synchronous motor has an inertia constant of four times that of the adjacent synchronous motor, and the ratio of ratings is one to four, the equivalent machine may be replaced during the transient period by its fixed pre-fault equivalent resistance. Again, the conclusion is valid for unity, 0.8 lag, and 0.8 lead power factors.
  7. If the equivalent synchronous motor's rating and inertia constant are both one-fourth of those of the adjacent machine, then for unity power factor pre-fault operation the equivalent machine may be replaced during the transient period by a fixed resistance equal to 6 per cent of its pre-fault equivalent resistance. For pre-fault power factors of 0.8 lagging and 0.8 leading, it may be replaced by 10 per cent and 15 per cent, respectively, of its pre-fault equivalent resistance.
  8. Incandescent lighting loads may be represented by their pre-fault resistances throughout the transient period.
  9. Neither the slimline nor the starter-type fluorescent lighting loads may be simulated by a single fixed impedance throughout the entire transient period. However, they may be represented by infinite impedances during the fault interval and by their pre-fault impedances during the post-fault period.
  10. The slimline fluorescent lamp power reaches steady values in about one cycle after an abrupt voltage drop from 1.00 per unit to 0.54 per unit and after an abrupt rise back to 0.69 per unit occurring 0.12 second later. The starter-type fluorescent lamp power requires about four cycles to reach a steady value after an abrupt voltage drop from 1.00 per unit to 0.47 per unit, and about 14 cycles for an abrupt voltage rise back to 0.79 per unit occurring about 0.2 second later.
  11. All of the above conclusions are valid for three-phase faults on the specified power system. For other types of faults involving the negative-sequence values, the steady-state negative-sequence impedances of the induction motor and of the synchronous motor may be used throughout the transient interval. The positive-sequence impedances are the same adjusted values as are used for the three-phase faults. For the lighting loads, the positive- and negative-sequence impedances are identical and equal to the values used for the three-phase faults.
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RADIOLOGICAL EFFECTS ON THE IMMUNE MECHANISM OF  
GENETICALLY DIFFERENTIATED STRAINS OF MICE  
EXPOSED TO *SALMONELLA TYPHIMURIUM*<sup>1</sup>Janice Stadler<sup>2</sup>

Department of Genetics

The influence of X-irradiation absorbed in three body regions and in the combinations of these regions has been measured on three subsequent responses: survival to radiation, natural resistance to disease, and ability to acquire immunity following contact with the disease agent, *Salmonella typhimurium*.

The experiment was designed as a factorial with five genetically differentiated strains of mice, S, Z, K, Q, and Balb/Gw; two sexes, three levels of radiation--320, 480, and 640 r; eight treatment groups, and one group at the 0 r level. At least 50 mice of each strain received like treatment. Strains and sexes were well balanced across the 25 treatment groups. The bodies of the mice were divided into three regions of equal body length, head or anterior third, mid, and rear or posterior third. Exposure of these three regions, the three combinations of two regions, and the two exposures involving the three regions, none and all, comprised the eight different regional body exposure treatments. Shielding of unexposed regions was with 1.8 inch lead. All mice were irradiated at  $46 \pm 3$  days of age in perforated plastic tubes. Radiation was given by a General Electric Maxitron operated at 250 pkv, 30 ma with 0.25 mm Cu + 1 mm Al filtration at an anode-mid-mouse distance of 47.5 cm and an average dose rate of 170 r/min.

A period of 15 days was allowed for the expression of direct effects of irradiation, with deaths recorded daily during that period. At 15 days post irradiation the mice were inoculated with *S. typhimurium*, 11C, to determine the effect of the previous X-irradiation on natural resistance to this disease. Infective doses were adjusted to the known susceptibilities of the strains; S, Z and K received 200,000; Q, 2000; and Ba, 200 organisms. Deaths were recorded daily for 21 days. A challenging inoculation, 100 times the initial infective dose, was given at 36 days post irradiation to measure the effect of the previous X-ray exposures on the ability of the mice to acquire immunity from contact with the disease. All the surviving animals were discarded 22 days after the challenge or 58 days post irradiation. Percentage survival and length of survival were the two scales of measurement for the effects of regional body irradiation on the three responses.

The sexes responded in like manner to X-irradiation, and to its effects on natural and acquired resistance.

The radiation resistance of the five strains of mice ordered from resistant to susceptible as S, Z, Q, K, and Ba. The exposures of the whole body to 320 r separated the two more sensitive strains, K and Ba, from the others. The five strains were separated by 480 r whole body. The 640 r whole body treatment was severe enough to overshadow the differences in genetic resistance between the strains. Only the four regional exposures at 640 r level which included the mid portion of the body proved sensitive to irradiation. The mid region was more sensitive than the head, rear, or head-rear, but less sensitive than the combined head-mid or mid-rear regions.

<sup>1</sup>Doctoral thesis number 1795, submitted May 29, 1956.

Chairman of Committee, John W. Gowen, Department of Genetics.

This work received assistance from the Atomic Energy Commission, Contract AT(11-1)107.

<sup>2</sup>B.A., University of Montana, Missoula. M.S., University of Wisconsin, Madison. Assistant Professor.

The interval of 15 days before infection with mouse typhoid did not allow complete recovery of the natural resistance mechanisms of the mice. The genetically determined disease resistance of each strain was of major importance in the reaction of given strains and diseases following the previous X-irradiation. The S strain with its high innate resistance proved the better host strain for measuring the dosage and regional effects of the X-irradiation in the response of natural resistance. The Balb/Gw strain was so susceptible to even 200 organisms of *S. typhimurium*, 11C, that information was gained only from the length of survival data. Strains Z and K with 45 and 39 per cent survival from typhoid infection, displayed little evidence of X-ray dosage effects--but even in these somewhat confined ranges the effects of different regional exposure was evident as measured by the degree or extent of recovery of their innate resistance levels. The sensitivity of the mid-region to irradiation persisted through 15 days--as shown by the greater effectiveness of mid-region exposures on natural resistance. The head regional exposures were more detrimental than those of the rear. The Q strain with only 19 per cent survival when infected with 2000 organisms reacted as did Z and K in showing regional effects but not dosage effects. The absence of dosage effects in Z, K, and Q mice was attributed to the limited range for expression due to the severity of the mouse typhoid or the selection due to the more severe X-ray treatments. The S, Z, K, and Ba strains maintained the same order in natural resistance to mouse typhoid as in radiation resistance; Q was resistant to radiation but was extremely susceptible to mouse typhoid.

After an interval of 36 days post irradiation the mice had largely recovered their ability to acquire immunity by previous contact with the disease. The four strains were able to withstand, at a higher survival level, a challenge dose 100 times larger than that of the initial infection. Radiation 36 days prior to the challenge did result in a slight lowering of the acquired resistance levels of the S, Z, K, and Q mice from that of the unirradiated controls, but dosage and regional effects were absent.

Quantitative estimations were obtained to determine the effects of exposures of the three separate regions on the subsequent responses. These effects were additive when any one portion was shielded. Whole body exposure resulted in decrease in survival above and beyond that accounted for by the combined effects of exposures to the head, mid, and rear regions.

Mortality due to irradiation in subsequent radiation sickness, in natural resistance to mouse typhoid and in acquired immunity to this disease for whole body exposure was only partially accounted for by the combined mortalities resulting from exposures to the different regions of the body. The effect of whole body exposure over and beyond that of the combined regional effects has been interpreted as a measure of the reaction when all cells of the body of the mouse had been exposed, or when all recovery potential had been affected.

The whole body effect was large and suggested that all cells may contribute to recovery regardless of the organ or system involved. As a consequence, protection of any cells of the body during exposure to radiant energy may stimulate recovery.

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SYNTHESES OF HYDROPHENANTHRENE KETONES<sup>1</sup>Travis E. Stevens<sup>2</sup>

Department of Chemistry

The purpose of this study was to develop general hydrophenanthrene syntheses that would yield intermediates useful for the total synthesis of the tricyclic diterpenes.

The base-catalyzed addition of ethyl acetoacetate to 4-(dichloromethyl)-4-methyl-1(4H)-naphthalenone yielded the enol of ethyl 3-keto-5-hydroxy-6,7-benzo-8-(dichloromethyl)-8-methylbicyclo[3.3.1]nonane-2-carboxylate. Acid-catalyzed hydrolysis of this enol gave 4-(dichloromethyl)-4-methyl-3-acetonyl-1-tetralone and 5-hydroxy-6,7-benzo-8-(dichloromethyl)-8-methylbicyclo[3.3.1]nonan-3-one. Hydrogenation in acid solution of either the diketone or the related hydroxy ketone gave 1-(dichloromethyl)-1-methyl-2-acetonyl-1,2,3,4-tetrahydronaphthalene. Treatment of the tetrahydronaphthalene with excess sodium triphenylmethyl gave trans-4a-methyl-4a,9,10,10a-tetrahydro-2(1H)-phenanthrene. Reduction of this phenanthrene yielded trans-4a-methyl-3,4,4a,9,10,10a-hexahydro-2(1H)-phenanthrene (I).

Potassium *t*-butoxide-catalyzed addition of 1-methyl-2-naphthol to methyl vinyl ketone gave the two racemic diastereoisomers of 1-methyl-5,6-benzo-8-acetylbicyclo[2.2.2]octan-2-one. No trace of the desired 4a-methyl-4,4a-dihydro-2(3H)-phenanthrene (II) could be found.

The acid-catalyzed addition of 1-methyl-2-naphthol to methyl vinyl ketone gave the desired phenanthrene II as well as the two bicyclic diketones previously isolated.

Addition of 1-methyl-2-naphthol to 4-chloro-3-buten-2-one gave 4-(1-methyl-2-naphthoxy)-3-buten-2-one. Catalytic hydrogenation of the naphthoxy butenone gave 4-(1-methyl-2-naphthoxy)-2-butanone. The naphthoxy butanone, on treatment with potassium *t*-butoxide, yielded 1-methyl-2-naphthol and the isomeric bicyclic octanones previously synthesized.

With potassium *t*-butoxide as catalyst, 1-methyl-2-naphthol reacted with methyl ethynyl ketone to give a mixture of 4-(1-methyl-2-naphthoxy)-3-buten-2-one, 4a-methyl-10a-hydroxy-4a,10a-dihydro-2(1H)-phenanthrene (III) and a small amount of an oil presumed to be 4a-methyl-2(4aH)-phenanthrene.

The hydroxy phenanthrene III was reduced to 4a-methyl-10a-hydroxy-3,4,4a,9,10,10a-hexahydro-2(1H)-phenanthrene, which was dehydrated to yield 4a-methyl-4,4a,9,10-tetrahydro-2(3H)-phenanthrene (IV).

Lithium in liquid ammonia reduction of IV gave the trans phenanthrene II, while catalytic hydrogenation gave predominantly cis-4a-methyl-3,4,4a,9,10,10a-hexahydro-2(1H)-phenanthrene (V). Catalytic hydrogenation of II also gave mainly V.

The ethylene ketal of the phenanthrene IV was prepared, and was isomerized to 4a-methyl-3,4,4a,10a-tetrahydro-2(1H)-phenanthrene ethylene ketal by base treatment. Hydrolysis of the ketal gave cis-4a-methyl-3,4,4a,10a-tetrahydro-2(1H)-phenanthrene (VI). The occurrence of cis ring fusion in VI was proven by catalytic reduction to the cis phenanthrene V.

<sup>1</sup>Doctoral thesis number 1682, submitted June 13, 1955.

Chairman of Committee, E. Wenkert, Department of Chemistry.

<sup>2</sup>A.B., Wayne State Teachers College, Wayne, Nebraska.

Fellow, Industrial Science Research Institute.

ACTION OF  $\beta$ -AMYLASE ON BRANCHED OLIGOSACCHARIDES<sup>1</sup>Russell E. Summer<sup>1</sup>

Department of Chemistry

Extensive action of macerans amylase using panose ( $\alpha$ -D-glucopyranosyl [1  $\rightarrow$  6]  $\alpha$ -D-glucopyranosyl [1  $\rightarrow$  4] D-glucose) as a co-substrate resulted in a series of oligosaccharides of varying molecular weight. These so-called branched oligosaccharides are analogous to the branch points found in amylopectin and glycogen. As such, they served as interesting model substrates in studying the action of hydrolytic enzyme,  $\beta$ -amylase.

A partial separation of the oligosaccharides was achieved by the technique of multiple ascent paper chromatography. The pentasaccharides, B<sub>5</sub>, with three possible isomers; the hexasaccharides, B<sub>6</sub>, with four possible isomers; and the heptasaccharides, B<sub>7</sub>, with five possible isomers were separated into three distinct fractions. Each of these fractions moved as a single spot on paper in the solvent system 3-4-6.

The three fractions were extensively degraded with  $\beta$ -amylase. The B<sub>5</sub> and B<sub>6</sub> groups definitely contained a resistant fraction, and the B<sub>7</sub> group probably contained a very small amount of a resistant fraction. R-enzyme, which is capable of splitting  $\alpha$ -1,6 glycosidic linkages, was used in studying the structure of the resistant fractions from B<sub>5</sub> and B<sub>6</sub>. The structure for the resistant B<sub>5</sub> was found to be  $\begin{array}{c} 0-0-0- \\ | \\ 0-0 \end{array}$ <sup>3</sup>, and the structure for the resistant

B<sub>6</sub> was found to be  $\begin{array}{c} 0-0-0- \\ | \\ 0-0-0 \end{array}$ . If there were a resistant B<sub>7</sub>, it probably had the structure  $\begin{array}{c} 0-0-0-0- \\ | \\ 0-0-0 \end{array}$ .

Isomaltose ( $\alpha$ -D-glucopyranosyl [1  $\rightarrow$  6] D-glucose) is also capable of acting as a co-substrate in the macerans amylase coupling reaction. This co-substrate is similar to panose in that it also contains two glucose units having a free hydroxyl group on carbon number 4. Since isomaltose contains one  $\alpha$ -1,6 linkage, it is possible to prepare a mixture of branched oligosaccharides which are analogous to the branch points in amylopectin or glycogen. The oligosaccharides prepared in this way were separated on paper into a tetrasaccharide group, B<sub>4</sub>, with three possible isomers; a pentasaccharide group, B<sub>5</sub>, with four possible isomers; and a hexasaccharide group, B<sub>6</sub>, with five possible isomers.

Each group was extensively degraded with  $\beta$ -amylase. Fractions of the B<sub>4</sub>, B<sub>5</sub>, and B<sub>6</sub> groups were resistant to  $\beta$ -amylase. The structure of each resistant fraction was studied, using R-enzyme and various methods based on the production of a flavazole derivative (1) of each fraction. It was found that the resistant B<sub>4</sub> fraction contained  $\begin{array}{c} 0-0- \\ | \\ 0-0 \end{array}$ , but may also have contained

$\begin{array}{c} 0-0-0- \\ | \\ 0 \end{array}$ . The resistant B<sub>5</sub> fraction contained  $\begin{array}{c} 0-0- \\ | \\ 0-0-0 \end{array}$  and  $\begin{array}{c} 0-0-0- \\ | \\ 0-0-0 \end{array}$ , while the resistant B<sub>6</sub> fraction contained  $\begin{array}{c} 0-0-0- \\ | \\ 0-0-0 \end{array}$ .

<sup>1</sup>Doctoral thesis number 1705, submitted August 4, 1955.

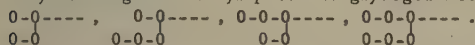
Chairman of Committee, Dexter French, Department of Chemistry.

<sup>2</sup>B.S., Michigan State College, East Lansing, Graduate Assistant, Agricultural Experiment Station.<sup>3</sup>0-signifies a glucose unit with its reducing group...0-0.. signifies two glucose units bonded with an  $\alpha$ -1,4 linkage. $\begin{array}{c} 0 \\ | \\ 0 \end{array}$ .. signifies two glucose units bonded with an  $\alpha$ -1,6 linkage.

A branched heptasaccharide, obtained from a salivary amylase digest of amylopectin (2), was separated on paper. This oligosaccharide, in contrast to the coupling products, consisted of a single compound of known structure, 0-0-0-0-. Although salivary amylase was able to break it down to maltose 0-0-0

and a B<sub>5</sub>, it was apparently completely resistant to the action of  $\beta$ -amylase.

It is apparent from these studies that a glucose unit on one chain has an effect on the ability of  $\beta$ -amylase to act on the other chain. From an overall examination of this work, the end groups one might expect to find in  $\beta$ -amylase-degraded amylopectin or glycogen would be of the following types:



The rate of  $\beta$ -amylase action on these various branched oligosaccharides was studied by analyzing for the increase in reducing power. A rate determination was also made for sweet corn glycogen (a water-soluble polysaccharide) and maltoheptaose. It was evident that as the enzyme approached the branch point, the rate diminished. Furthermore, it appears that the attainment of an absolute limit dextrin in a natural molecule is an impractical goal. The rate, on a comparative basis, of  $\beta$ -amylase action for various substrates is recorded in Table 1.

Table 1. Relative rates of  $\beta$ -amylase on glycogen, maltoheptaose, and the branched oligosaccharides.

Substrate	Relative rate
Maltoheptaose	1.000
Sweet corn glycogen	0.620
Panose coupled products B <sub>7</sub>	0.370
Panose coupled products B <sub>6</sub>	0.095
Panose coupled products B <sub>5</sub>	0.002
Isomaltose coupled products B <sub>6</sub>	0.223
Isomaltose coupled products B <sub>5</sub>	0.164
Isomaltose coupled products B <sub>4</sub>	0.013

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ECOLOGY OF THE CABBAGE ROOT MAGGOT,  
*HYLEMYA BRASSICAE* (BOUCHE), IN SOUTHERN ALBERTA<sup>1</sup>George Edward Swailes<sup>2</sup>

Department of Zoology and Entomology

Selected aspects of the ecology of *Hylemya brassicae* (Bouché), a serious pest of rutabagas in southern Alberta, were studied from 1953 to 1955 in field and laboratory experiments in Lethbridge, Alberta.

Detailed oviposition records from Cruciferae transplanted into the field were taken for July, August, September, and October for three years. Peak populations of eggs appeared in late August and early September except in 1954 when high rainfall in August reduced the late summer populations and resulted in the peak of eggs occurring in mid-August.

The relative attractiveness to oviposition of Early Snowball cauliflower, Copenhagen Market cabbage, Laurentian rutabaga, and Purple Top White Globe turnip was tested in four latin-square plots in the field. Cauliflower was found to be the most attractive in two plots and turnips in one plot. The greatest proportion of eggs was laid on turnips during the early season and on cauliflower during the late season. Cauliflower appeared to retain its attractiveness over the longest period. Attractiveness was attributed to a chemical constituent as plant color, texture, growth habit, and environment as influenced by growth habit were all shown to have no influence on oviposition. Purple Top White Globe turnip was significantly more attractive than rutabaga in laboratory tests. However, seven varieties of rutabaga, namely, Lord Derby, Wilhelmsburger, Laurentian, Westbury, Selected Purple Top, Ditmar's Bronze Top, and Canadian Gem showed no differences in egg counts when tested in cages in the greenhouse. A test with these same varieties except Lord Derby in the field showed no differences in numbers of eggs. As a result of the preference demonstrated in the laboratory and in the field, turnips were used as a trap crop to protect rutabaga; however, the effect of the preferred host was apparently masked by the high population of adults competing for oviposition sites or the early maturity of the turnips which lost their attractive properties before the peak egg-laying period had been completed.

Observations on eggs placed on moist blotter in petri dishes in the laboratory showed that eggs were killed by constant 5°C or an exposure of two hours to 36°C. The incubation period varied from an average of 65.9 hours at 25°C to 293.1 hours at 10°C. The optimum constant temperature was 20°C where 93.6 per cent of the eggs hatched. The longest and shortest period of development for one individual were 326.5 hours at 10°C and 56.5 hours at 30°C.

Larval development times at constant temperature with Laurentian rutabaga as the food host ranged from an average of 21 days at 25°C to an average of 75 days at 10°C. The larvae died at constant 30°C. Optimum survival was 47 per cent and occurred at 15°C. Larval populations observed at weekly intervals on 24 plants in the field in 1955 peaked on August 10 and high populations persisted until the end of the experiment in mid-October.

There was 60 per cent or higher survival of larvae reared on seven rutabaga varieties in the laboratory. However, on six of these varieties in the field the numbers of larvae varied greatly. Because the numbers of eggs on the varieties were not significantly different it was concluded that some varieties, particularly Wilhelmsburger, possessed ability to withstand first

<sup>1</sup>Doctoral thesis number 1787, submitted May 18, 1956. Chairman of Committee, Oscar E. Tauber, Department of Zoology and Entomology.

<sup>2</sup>B.S.A., University of Manitoba, Winnipeg, Canada. M.S., Colorado Agricultural and Mechanical College, Fort Collins.

instar penetration of the epidermis. In two varieties, Westbury and Laurentian, mature plant resistance to larval survival after establishment was indicated by failure of pupal populations to peak following the larval peaks.

Pupation averaged 41 days at 25°C and 183 days at 15°C. Emergence at 15°C was considered near optimum as it followed a nearly normal curve with about two-thirds of the individuals developing in 140 to 200 days. Apparently 25°C was near the high lethal temperature as emergence was low and sporadic.

Emergence of adults in the field began on May 11 in 1954 and May 18 in 1955 with a peak in early June both years, and a second peak in mid-July in 1955. First generation pupae collected from the end of July to the middle of August emerged in 30 days when held at 20°C, but an increasing number of those pupae collected after mid-August were apparently in diapause.

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### SYNTHESIS AND ORIENTATION OF SOME DERIVATIVES OF THIANTHRENE<sup>1</sup>

Dhairyasheel R. Swayampati<sup>2</sup>

Department of Chemistry

Thianthrene has been shown to metalate with *n*-butyllithium in the 1-position (1). From the 1-thianthrenyllithium were obtained 1-thianthrene-carboxylic acid, m.p. 224-225°, and 1-aminothianthrene, m.p. 121-122°, in greater purity than had been previously obtained (1). The method of preparation of 1-hydroxythianthrene (2) was modified to give an improved yield of 18.3 per cent of the product. Treatment of 1-thianthrenyllithium with triphenylchlorosilane and with tri-*n*-butyl borate gave 1-thianthrenyltriphenylsilane, m.p. 190.5-191.5°, and 1-thianthreneboronic acid, m.p. 147-148°, respectively.

The reaction between thianthrene-5-oxide and *n*-butyllithium at low temperatures followed by carbonation gave dibenzothiophene as the main product along with small amounts of thianthrene and 2,2'-dicarboxydiphenyl sulfide, while methyllithium reduced the sulfoxide at the reflux temperature of ether to give a 60 per cent yield of thianthrene.

Alkylmagnesium bromides cleaved thianthrene-5-oxide at low temperatures to yield 2-alkylsulfinyl-2'-carboxydiphenyl sulfides. Thus, 2-ethylmagnesium bromide and 2-*n*-butylmagnesium bromide gave 2-ethylsulfinyl-2'-carboxydiphenyl sulfide, m.p. 158-159° (decomp.), in 29 per cent yield, and 2-*n*-butylsulfinyl-2'-carboxydiphenyl sulfide, m.p. 149-149.5° (decomp.), in 50 per cent yield, respectively. Methylmagnesium iodide did not react with the sulfoxide under the experimental conditions.

Thianthrene-5-dioxide was metalated with *n*-butyllithium at low temperatures to yield, upon carbonation, 4-carboxythianthrene-5-dioxide, m.p. 256-257°, and 4,6-dicarboxythianthrene-5-dioxide, m.p. 364 (decomp.). Oxidation of the monocarboxylic acid with 30 per cent hydrogen peroxide gave a product which was identical with the 1-carboxythianthrene-5,10-tetraoxide obtained by the oxidation of 1-thianthrenecarboxylic acid.

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<sup>1</sup>Doctoral thesis number 1701, submitted July 14, 1955.

Chairman of Committee, Henry Gilman, Department of Chemistry.

<sup>2</sup>B.Sc., Bombay University, India. M.S., Southern Methodist University, Dallas, Texas.

Associate, Industrial Science Research Institute.



The attempted metalations of thianthrene-5,10-dioxide and of thianthrene-5,10-tetraoxide with *n*-butyllithium were unsuccessful.

Thianthrene-5,5,10-trioxide was cleaved by *n*-butyllithium at the low temperature of  $-70^{\circ}$  to give, upon carbonation, a 5 per cent yield of dibenzothio-*phene*-5-dioxide and a 16.6 per cent yield of 2,2'-dicarboxydiphenyl sulfone, identical with the product prepared by Gilman and Esmay (3). The reaction resembles that of *n*-butyllithium with thianthrene-5-oxide.

2-Thianthrenecarboxylic acid, m.p.  $227-228^{\circ}$ , was obtained from 2-bromothianthrene by a halogen-metal interconversion with *n*-butyllithium and subsequent carbonation of the reaction mixture. The structure of the 2-bromothianthrene was established by its conversion to the aminothianthrene which was identical with the 2-aminothianthrene obtained by Keats' method (4).

1-Chlorothianthrene, m.p.  $85-85.5^{\circ}$ , was prepared from 1-aminothianthrene by the Sandmeyer reaction. The action of a molar equivalent of bromine on thianthrene and of hydrobromic acid on thianthrene-5-oxide resulted in the formation of fair yields of 2-bromothianthrene, m.p.  $89-90^{\circ}$ . An isomeric mixture of 2,7- and 2,8-dibromothianthrene was obtained by the action of two molar equivalents of bromine on thianthrene, of hydrobromic acid on thianthrene-5,10-dioxide, and of a molar equivalent of bromine on thianthrene-5-oxide. Thianthrene-5-dioxide did not react with bromine under the experimental conditions. The action of hydrobromic acid upon thianthrene-5,5,10-trioxide did not proceed beyond reduction to thianthrene-5-dioxide. The reductive bromination of sulfoxides appeared to proceed through the initial reduction of the sulfoxide to the heterocycle followed by the electrophilic attack by the liberated bromine, which was evidenced by the color of the solution of the vapor above the solution. The presence of the deactivating sulfone group would explain why thianthrene-5,5,10-trioxide did not undergo reductive bromination with hydrobromic acid.

The following compounds were prepared by oxidation with 30 per cent hydrogen peroxide; 2-bromothianthrene-5,10-tetraoxide, m.p.  $226-227^{\circ}$ ; 2-carboxythianthrene-5,10-tetraoxide, m.p.  $302-303^{\circ}$ ; 1-carboxythianthrene-5,10-tetraoxide, m.p.  $307-308^{\circ}$ ; 1-chlorothianthrene-5,10-tetraoxide, m.p.  $242^{\circ}$ ; 2-*n*-butylsulfonyl-2'-carboxydiphenyl sulfone, m.p.  $159.5-160.5^{\circ}$  (decomp.). Oxidation of thianthrene with chlorine in hot 90 per cent acetic acid gave excellent yields of thianthrene-5,5,10-trioxide, m.p.  $221.5-222.5^{\circ}$ .

Reduction of the corresponding sulfoxides with zinc and 90 per cent acetic acid or hydrobromic acid gave the following compounds: thianthrene-5-dioxide, m.p.  $168-169^{\circ}$ ; 2-ethylmercapto-2'-carboxydiphenyl sulfide, m.p.  $195-196^{\circ}$ ; 2-*n*-butylmercapto-2'-carboxydiphenyl sulfide, m.p.  $142^{\circ}$ . Reduction of 2-nitrothianthrene with zinc and 90 per cent acetic acid results in the formation of 2-acetamidothianthrene (4). Direct reduction of the 2-nitrothianthrene to 2-aminothianthrene was accomplished by treatment with ethanolic hydrochloric acid and tin. Treatment of the 2-aminothianthrene with acetic anhydride gave 2-acetamidothianthrene.

1-Thianthreneoxyacetic acid, m.p.  $174-175^{\circ}$ , and its ethyl ester, m.p.  $90-90.5^{\circ}$ , were obtained from 1-hydroxythianthrene by the action of chloroacetic acid and ethyl bromoacetate, respectively. The two products may have interesting possibilities in the field of plant hormones.

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EFFECTS OF HERBICIDES ON MITOCHONDRIAL  
ENZYME SYSTEMS<sup>1</sup>Clayton M. Switzer<sup>2</sup>

Department of Botany

Although the use of chemicals for weed control is widespread, knowledge concerning the mechanism of action of these herbicides is meager or lacking. Many diverse plant processes have been shown to be affected but the site of action of these materials has not been pin-pointed. The idea that a major site of action may exist in the oxidative or phosphorylative systems seemed to be a good working hypothesis. These systems have been shown to be located in discrete cytoplasmic particles called mitochondria which may be isolated in active form. It was thought that such active particles would provide a system for the *in vitro* study of the effects of herbicides on respiration.

Etiolated soybean hypocotyls were macerated in a chilled mortar with cold quartz sand and hypertonic sucrose-phosphate solution. The brei obtained was filtered through cheesecloth, then centrifuged at 500 times gravity for 5 minutes to remove cellular debris and sand. The supernatant was spun in the high speed head of a refrigerated centrifuge at 10,000 times gravity for 15 minutes. The precipitate in each tube was resuspended in cold sucrose-phosphate solution and centrifuged again at 10,000 times gravity. The particles sedimented by this second high-speed spinning were resuspended and transferred to a glass homogenizing tube. After homogenization, aliquots of this suspension were added to Warburg flasks for determination of oxidative activity. All values for gas exchange were calculated from manometer readings 30 minutes after closing the stop-cocks, and were expressed as microliters per mg nitrogen per hour.

Soybean particles were capable of oxidizing all Krebs cycle intermediates tested, although fumarate and oxaloacetate were oxidized relatively slowly. Judging from respiratory quotient (r.q.) values, most of these intermediates were oxidized completely to carbon dioxide and water. However, succinate oxidation proceeded consistently with an r.q. of about 0.3, indicating that a large proportion of this substrate was incompletely oxidized.

Oxygen uptake in the presence of succinate, pyruvate, or ketoglutarate was increased two to four times by the addition of ATP,  $MgSO_4$ , and cytochrome c. Maximum activity was obtained when both sucrose and phosphate were added to the grinding and suspending media, and when the reaction mixture was buffered near pH 7.0. Endogenous oxidation was reduced 50 per cent by one washing and at the same time the oxidation of exogenous substrate was increased two to three times.

In experiments in which the phosphorylating ability of isolated soybean mitochondria was studied, the amount of inorganic phosphate in the reaction mixture at zero time and at the end of the experiment was determined colorimetrically. The difference between these two determinations was considered to represent the amount of inorganic phosphate esterified by the enzyme system. The number of micromoles of phosphate thus esterified, divided by the number of microatoms of oxygen taken up during the same time (P:O ratio) gives an indication of the efficiency of the system in preserving the energy liberated during oxidation. Average P:O ratios of 0.4, 0.8, and 0.9 were obtained without added hexokinase or fluoride, for succinate, pyruvate, and

<sup>1</sup>Doctoral thesis number 1702, submitted July 14, 1955.

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M.S.A., University of Toronto, Toronto, Ont., Canada.

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ketoglutarate, respectively. These ratios were increased to 0.8, 1.2, and 1.5 by the addition of exogenous hexokinase. In all cases, sodium fluoride decreased oxygen uptake 30 to 40 per cent without affecting P:O ratios. Dinitrophenol and dichlorophenol were shown to uncouple phosphorylation from ketoglutarate oxidation.

In experiments designed to study the effects of various herbicides and related chemicals on oxidation by soybean mitochondria, these materials were added to the reaction mixture in the Warburg flasks. All chemicals tested inhibited oxidation at high concentrations. Some of these effects at concentrations above 0.1 M were probably brought about through osmotic changes. In most cases, however, inhibition must have been caused by a toxic action of the added chemical. Triiodobenzoic acid (TIBA) was the most active inhibitor of oxidation tested. In general, none of the chemicals tested stimulated respiration in the presence of added substrate. One exception was the stimulation of oxygen uptake by 2,4-dichlorophenoxyacetic acid (2,4-D) in systems containing low added inorganic phosphate.

The herbicide 2,4-D was investigated more extensively than any other chemical. The effects of pretreatment and *in vitro* treatment with 2,4-D were studied in relation to phosphate uptake as well as oxidation. Both processes were inhibited *in vitro*, with phosphorylation inhibited to the greater extent. Pretreatment of hypocotyls with  $5 \times 10^{-4}$  M 2,4-D increased the oxidative and phosphorylative ability of isolated particles. This increased activity was probably related to changes in the morphology of the tissue, leading to isolation of more-active particles, rather than to changes in the mitochondrial complex of enzymes *in vivo*. Analysis of the 2,4-D for dichlorophenol (DCP) contamination showed that the results obtained with 2,4-D could not have been caused by the low concentration of DCP present.

All of the chemicals tested appeared to inhibit *in vitro* respiration by means of a general inhibition of mitochondrial enzymes than by a specific effect on certain enzymes. While quantitative comparisons between the effects of various concentrations of chemicals on plant particles *in vitro* and *in vivo* are difficult, it is considered that the results obtained by treatment with the various chemicals are qualitatively comparable.

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## SPECTROGRAPHIC DETERMINATION OF OXYGEN IN METALS<sup>1</sup>

Raymond W. Tabeling<sup>2</sup>

Department of Chemistry

Minute quantities of oxygen can drastically affect the physical properties of metals causing loss of ductility, increased hardness, and grain refinement. Present methods for this determination are time consuming and require elaborate equipment. A spectrographic approach to this problem seemed promising because of its inherent speed, sensitivity, and precision at low concentrations.

Elimination of atmospheric interference was accomplished by constructing an excitation chamber that could be readily evacuated. A rare gas purification train was developed to supply oxygen-free gases when excitation was performed in a gaseous atmosphere.

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<sup>1</sup>Doctoral thesis number 1849, submitted December 8, 1955.

Chairman of Committee, Velmer A. Fassel, Department of Chemistry.

<sup>2</sup>B.S., Xavier University, Cincinnati, Ohio. M.S., Iowa State College, Ames. Research Assistant, Institute for Atomic Research.

Excitation in a vacuum proved unsuccessful, because a source unit capable of supplying the 100,000 volts necessary to initiate a spark discharge in a vacuum was not available. Excitation with a vacuum arc also failed, because the condensation of the metal vapor from the discharge quickly coated the optical window and no spectroscopic observations could be made.

Using the National Bureau of Standards steel standards, a spark discharge in an oxygen-free atmosphere was found to provide insufficient sensitivity. An overdamped condenser discharge as obtainable from the Multisource unit provided a sensitivity of 0.06 per cent oxygen in steel in an argon atmosphere, and in a hydrogen atmosphere a sensitivity of 0.02 per cent was found.

Vacuum fusion conditions were approximated spectrographically by fusing a one gram steel sample in a carbon electrode at 20 amperes. Any oxides present were reduced to carbon monoxide which was liberated into the argon atmosphere of the chamber. The intensity ratio of  $O_{7771}$  to  $A_{7891}$  was measured to determine the amount of oxygen originally present in the sample. Experiments proved that all of the oxygen was reduced and liberated in less than one minute and that argon was an ideal internal standard. A sensitivity of approximately 0.0005 per cent was obtained for this method, and an average precision of 10 per cent over the concentration range of 0.002 per cent to 0.106 per cent oxygen in steel was found. Time per analysis was approximately 15 minutes. A similar spectrographic method was also successfully applied to the determination of oxygen in nickel.

The principal cause of the oxygen blank found in this determination was to the outgassing of the excitation chamber during the arc exposures. Oxygen blank arising from this source was minimized by heating the chamber with high current arcs followed by evacuation. The oxygen blank arising from absorbed gases in the carbon electrodes was eliminated by a preliminary outgassing at 1000°C in a high vacuum.

The determination of oxygen in lanthanum was successfully accomplished by providing a nickel bath to facilitate the reduction of the oxides. A two-gram cup was machined from low oxygen nickel and the lanthanum sample (0.5 gm) was placed in this cup. The whole assembly was then placed in a carbon electrode and arced at 30 amperes.

This spectrographic method for the determination of oxygen in metals appears to have the wide applicability of vacuum fusion techniques in addition to increased speed, sensitivity, and precision.

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#### DECAY SCHEME OF $Yb^{169}$

James H. Talboy, Jr.<sup>2</sup>

Department of Physics

The radiations following the K-capture in  $Yb^{169}$  have been studied with an intermediate-image beta-ray spectrometer, and a two-channel scintillation spectrometer. Seventeen gamma rays have been observed, either by their internal conversion or photoelectric lines, or both. The energies of these transitions are: 10.3, 14.8, 21.1, 59.1, 65.0, 77.7, 81.0, 92.5, 110.0, 119.5, 132.8, 159.9, 176.8, 198.8, 217.8, 265.2, and 308.6 kev.

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<sup>1</sup>Doctoral thesis number 1766, submitted March 2, 1956.

Chairman of Committee, E. N. Jensen, Department of Physics.

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Graduate Assistant, Institute for Atomic Research.

With coincidence measurements made with the two machines, and the experimental determination of some internal conversion coefficients, a decay scheme has been proposed. This scheme has levels at 10.3, 120.3, 141.4, 318.2, 340.1, 383.2, 399.1, and 478.1 kev above the ground state. The levels at 10.3, 120.3, 141.4, and 340.1 kev are members of one rotational family having spins  $3/2$ ,  $5/2$ ,  $7/2$ , and  $9/2$ , respectively, and even parity. The agreement with the theory of nuclear rotational levels is good. The levels at 318.2 and 383.2 kev are assigned spins of  $9/2$  and  $11/2$ , respectively, with even parity. It is not possible to make any definite assignment of spin or parity for the levels at 399.1 and 478.1 kev.

On the basis of delayed coincidence measurements the metastable state is assigned to the 383.2-kev level. The half-life of this state is measured to be  $0.658 \pm 0.024$  microseconds.

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### GROWTH AND FATTENING STIMULATION IN LAMBS AND SWINE BY CERTAIN ADROGENIC AND ESTROGENIC COMPOUNDS<sup>1</sup>

Bruce R. Taylor<sup>2</sup>

Department of Animal Husbandry

One hundred twenty pigs and 184 lambs were used in a study of five synthetic hormone compounds in the production of quality, wholesome pork and lamb, and in observing the effects of certain endocrine stimulants on glands and tissues of the body.

Levels of stilbestrol of 0, 5, 10, 20, 40, 80, 160, 320, 640, and 1280 mcg per pound of ration were fed in two experiments to growing-finishing pigs from 33 to 200 pounds weight. Rate of gain, feed intake, and feed efficiency were not significantly affected by the feeding of stilbestrol, but levels of either 10, 80, or 160 mcg per pound of feed increased rate of gain to a greater extent than the other levels fed. Live probe measurements, dressing percentage, and cooler shrink showed no significant differences due to treatment. Evidence of stimulation was shown by enlargement of the vulva and teats in gilts at levels of 160 mcg or more of stilbestrol per pound of feed. These levels also increased the size of the rudimentary teats in barrows. Ovary size was depressed by stilbestrol in all but the 10 mcg per pound level. Follicles were decreased in both size and number by stilbestrol. The diameter of the cervix and the weight of the reproductive tract were significantly increased by treatment and the diameter of the cervix was correlated with level of feeding of stilbestrol.

Testosterone propionate, methyl testosterone, stilbestrol, and a combination of progesterone and estradiol were either fed or implanted, singly and in various combinations, to ewe lambs in four experiments. In the first trial, conducted in the December to March feeding period, an injection of 3.3 mg of testosterone propionate per 100 pounds live weight per day increased rate of gain by 38 per cent over control lambs. Methyl testosterone fed at levels of either 2.41 or 12.07 mg per lamb per day increased gains by 16 per cent. Feed efficiency favored the treatments with the lambs injected with testosterone propionate requiring 19 per cent less feed per unit of gain. Carcass

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<sup>1</sup>Doctoral thesis number 1708, submitted August 9, 1955.

Chairman of Committee, Wise Burroughs, Department of Animal Husbandry.

<sup>2</sup>B.S., Kansas State College, Manhattan. M.S., *ibid*.

Associate Professor.



grades and dressing percentages were highest in the group fed the higher level of methyl testosterone and lowest in the group treated with testosterone propionate. Testosterone propionate significantly increased the size of the thyroid, whereas the higher level of methyl testosterone reduced thyroid size. In subsequent experiments these results could not be duplicated with ewe lambs.

In three trials conducted at slightly different seasons of the year and all using an 11.5 per cent protein ration, stilbestrol had either no effect or caused a significant depression in feed intake and rate of gain. Levels of stilbestrol from 0.003 to 2.68 mg per lamb per day were used.

A commercial implant containing progesterone and estradiol significantly increased rate of gain, reduced the feed required per unit of gain, and increased the daily consumption of corn, but not of total feed. This treatment lowered carcass grades significantly and 50 per cent of the carcasses were classified as yearlings because of shape, and whiteness of the bones, and the ossification of the break joint. Excessive riding was evident in the group implanted with progesterone and estradiol by the fourth day after implantation and 20 per cent of the lambs accepted a vasectomized ram at least once during the first half of the 71-day trial.

In Experiment 4, the progesterone-estradiol implant enlarged uterine size significantly and reduced the size and number of follicles, but had no effect on weight of the ovaries. Stilbestrol, on the other hand, increased uterine size, decreased ovary size, and was detrimental to follicle size and development. Testosterone propionate had no effect on uterine size, but increased both the weight of the ovaries and the number of follicles measuring 2 mm or more in diameter. Shorn lambs implanted with 30 mg of testosterone propionate gained 27 per cent faster than their woolled pen mates, but failed to gain significantly more than either shorn or woolled control lambs.

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#### INHERITANCE OF POLLEN RESTORATION AND TRANSMISSION OF CYTOPLASMIC STERILITY IN POPCORN<sup>1</sup>

Walter Ivan Thomas<sup>2</sup>

Department of Agronomy

Crosses were made between 9 popcorn inbred lines not capable of restoring pollen fertility and Tx127C and K55, two dent corn inbreds that restore pollen fertility to cytoplasmic male sterile lines. The BC<sub>1</sub> plants derived from backcrossing to the popcorn inbreds were used as male parents in test crosses to cytoplasmic male sterile stocks to determine the inheritance of pollen fertility restoration. Tassels of individual plants in test-cross progeny rows planted at two dates were examined and each row was classified for pollen restoration. The tassels of S<sub>1</sub> progeny of crosses between 12 converted cytoplasmic male sterile popcorn inbreds and K55 and Tx127C were also classified for pollen restoration. It was concluded from these data that pollen restoration was determined by a single dominant gene. In one cross between popcorn inbred 28 and Tx127C, the results did not give a satisfactory fit to a monogenic ratio.

A cross was made between Tx127C and K55. Plants in the F<sub>2</sub> were used in

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<sup>1</sup>Doctoral thesis number 1734, submitted November 30, 1955.

Chairman of Committee, I. J. Johnson, Department of Agronomy.

<sup>2</sup>B.S., Iowa State College, Ames. M.S., *ibid*.

Graduate Assistant, Agricultural Experiment Station.

test crosses to cytoplasmic male sterile stocks. All test-cross progeny rows were homozygous fertile and it was concluded that the genes for pollen restoration in these two lines were allelic.

Some inbred popcorn lines in the process of conversion to cytoplasmic male sterility exhibited partial pollen fertility which decreased with additional backcrossing, even though no selection was made in the recurrent popcorn lines. These results were interpreted as an initial interaction of modifier genes in the cytoplasmic sterile stock and the popcorn lines which diminished as the proportion of the nonrecurrent parent genotype became less in successive backcrosses.

A survey was made to discover possible new sources of pollen fertility restoration to cytoplasmic male sterile stocks among existing popcorn lines in the breeding nursery. Among the 78 lines tested, one was found to be as fully effective as either dent corn, inbreds Tx127C or K55. Preliminary data suggest that fertility restoration in this line may be conditioned by a single dominant gene.

Microscopic analyses were made of pollen from progeny of converted cytoplasmic sterile popcorn lines crossed with a pollen restorer and of pollen from the normal popcorn lines. No apparent differences were found, suggesting that pollen fertility restoration had been fully effective. Further microscopic analysis of pollen was made from plants varying in expression of partial fertility restoration. The percentage of stainable pollen was found to be progressively higher with increased numbers of fertile florets per tassel.

Fertile plants in segregating progeny rows of 8 converted cytoplasmic male sterile stocks crossed by single crosses of the 8 popcorn lines x pollen restorer were backcrossed by the recurrent nonpollen restoring parent for two generations. In this manner, simultaneous addition of cytoplasmic male sterility and pollen fertility restoration could be made, since the cytoplasmic male sterile background would serve to identify plants heterozygous for pollen fertility restoring genes. Data from this study indicated that this method of transferring cytoplasmic male sterility and pollen fertility restoration was as effective as a backcrossing program in which the two characters were added in separate populations.

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#### CONSTRUCTION AND VALIDATION OF A TEST OF SKILLS IN FARM MECHANICS FOR VOCATIONAL AGRICULTURE PUPILS<sup>1</sup>

Marvin D. Thompson<sup>2</sup>

Department of Vocational Education

This investigation involved an attempt to develop sample test procedures of manipulative skills for vocational agriculture pupils in farm mechanics, to evaluate these procedures, and to revise the test instruments to a workable form for use by teachers of vocational agriculture.

Sample jobs involving simple skills in farm mechanics were selected as presenting typical evaluation problems. Jobsheets and evaluative instruments were developed. Jobs selected as suitable for use in the testing program were:

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<sup>1</sup>Doctoral thesis number 1736, submitted December 1, 1955. Chairman of Committee, John B. McClelland, Department of Vocational Education.

<sup>2</sup>B.S., Iowa State College, Ames. M.S., *ibid*. Instructor.

1. Making a framing square hanger.
2. Making a funnel pattern.
3. Turning an eye for an eyebolt.
4. Cutting threads.
5. Making a butt weld.
6. Replacing a ledger plate.

Directions given in the job sheets were similar to those recommended by authors of farm mechanics texts. The evaluative techniques consisted of two types. One involved a system of measurement using scales or gauges to determine variations in dimensions, and the other involved a subjective evaluation in the form of choosing an appropriate number on five-point descriptive scales to indicate variations in quality.

Twenty-one teachers of vocational agriculture from departments located in various areas in Iowa participated in the study. The tests were given to pupils in classes having received some previous instructions in the skills to be tested. Usable job products were obtained from 918 pupils. Each job product received four evaluations. One evaluation was by the local vocational agriculture teacher and three were by teachers of farm mechanics on the staff of the Department of Agricultural Engineering of Iowa State College with previous experience in teaching farm mechanics to high school pupils.

A multiple coefficient of correlation was obtained for each of five jobs for which sufficient data were available. The correlations were between scores on the various factors involved in the instruments and the over-all ratings. These correlations were: 0.8153 for making the framing square hanger, 0.7529 for making a funnel pattern, 0.7474 for turning an eye for an eyebolt, 0.8652 for cutting threads, and 0.9502 for making a butt weld.

An analysis of covariance for scores given in each of the aforementioned five jobs was computed. Controls were made on the evaluators of the job product and on the class levels of the pupils tested. In each of the five jobs highly significant differences were found between the scores given by evaluators for the quality of the job products. In four of the five jobs these differences were due to the fact that the local agricultural instructors placed a better quality rating on the job product than did the other three evaluators. The three evaluators who had had recent experience in teaching college classes in farm mechanics may have been influenced in their evaluations by the quality of work performed in college classes.

With three of the five jobs tested there were significant differences existing between the class levels of the pupils tested and scores for the quality of the completed job product. In general, freshman and sophomore pupils were not as proficient as junior and senior pupils in constructing job products receiving high quality scores.

The test instruments were revised in order to obtain a form usable by the vocational agriculture instructor. Variables were dropped which made no contribution to the scoring devices and weights were determined for each variable in order to obtain a simple scoring scheme.

This investigation has described a procedure for evaluating shop products involving manipulative skills. The study should suggest possible devices or techniques for evaluating other skills which are taught in farm mechanics or in other shop courses.

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GROWTH OF PLANTATION BLACK WALNUT IN SOUTHEASTERN IOWA  
AS RELATED TO CERTAIN SOIL PROPERTIES<sup>1</sup>George Willis Thomson<sup>2</sup>

Department of Forestry and of Agronomy

The purpose of this study was to determine the soil factors causing the pronounced differences in growth rate exhibited by 15 to 17 year old black walnut, *Juglans nigra* L., plantations in southeastern Iowa.

The soils studied were silt loams derived from loess over Kansan till and were generally located on bottomland benches and lower slopes. The majority of the trees studied was found on soils very light in color, pH 4.5 - 6.0 in reaction, and characterized by pronounced mottling and the presence of reddish-brown concretions.

The experimental work was carried out according to a threefold plan:

1. Fifty-nine plots were selected for initial observation and study, and from these plots eighteen were drawn for more intensive study of soil chemical and physical properties.
2. Black walnut leaves were collected from 28 plots and foliar analyses were made for nitrogen, phosphorus, potassium, calcium, and magnesium.
3. Fertility tests were conducted in the field and in pots in the nursery. Calcium and potassium were applied in a 2 x 2 factorial design in the field using 15 replicates. A 4 x 2 factorial design was employed to test the response of black walnut seedlings to the addition of nitrogen, phosphorus, potassium, and calcium in a pot test using three replications.

In the evaluation of the established plantations a series of site index curves was established. It was found that each of the four major site classes exhibited a different height-age relationship in respect to the shape of the site index curve.

Of the physical soil characteristics measured, only depth of soil above an impervious layer and the 10 YR Munsell color "values" for dry, surface soil were significantly correlated with site index. No significant relationship was found between site index and topographic position, aspect, soil texture, volume weight, pore volume, specific gravity, field moisture capacity, and degree or color of subsoil mottling.

Site index was found to vary directly, and with high statistical significance, with both surface and subsurface soil pH.

Total exchangeable bases and per cent of base saturation of the surface soil were directly correlated linearly with site index. Significance was at the 1 per cent probability level. Total base exchange capacity of the surface soil was not statistically correlated with site index.

The regressions of site index on nitrifiable nitrogen, exchangeable potassium, and exchangeable calcium in the surface soil were found to be linear, direct, and highly significant.

Site index decreased significantly with increasing amounts of soluble iron, 5 per cent probability, and soluble aluminum, 1 per cent probability.

<sup>1</sup>Doctoral thesis number 1798, submitted May 31, 1956.

Chairmen of Committee, A. L. McComb, Department of Forestry, and W. H. Pierre, Department of Agronomy.

<sup>2</sup>B.S., Iowa State College, Ames. M.S., *ibid.* Assistant Professor.

The amounts of calcium and potassium in walnut leaves were significantly correlated with the amounts of exchangeable calcium and potassium found in the surface soil. Foliar nitrogen was not statistically correlated with the nitrifiable nitrogen in the surface soil.

Site index was found to be significantly correlated with foliar calcium, magnesium, potassium, and nitrogen in a positive and linear manner. Site index decreased as foliar phosphorus increased, but the linear regression was just short of statistical significance.

Partial regression coefficients strongly suggested that potassium and, to a lesser degree, calcium were the nutrient elements most limiting to good walnut growth in the soils studied.

Results from the addition of potassium and calcium to black walnut saplings in the field were not conclusive at the end of one growing season although there appeared to be a positive response to the addition of potassium.

In the pot test with black walnut seedlings grown on one of the poor, site class IV soils it was found that the effect of all nutrients added, except potassium, was to improve growth when the untreated check was used as the basis for comparison. Potassium significantly increased the moisture content of walnut seedlings and when treatment results were arrayed in diminishing order potassium was in the lowest quartile in terms of plant height, total green weight, total dry weight, dry weight of roots, dry weight of tops, and root top ratio. Severe necrosis accompanied the application of potassium.

In the pot test calcium was in the top quartile of arrayed values for plant height, total plant green weight and dry weight, and dry weight of roots or tops.

Magnesium seemed to improve growth in dry weight of walnut seedlings much as did calcium.

Nitrogen, phosphorus, and the combinations of other nutrients tested in the pots failed to produce statistically significant improvement in the growth of walnut seedlings.

In the area studied, a number of interrelated factors appears to limit, to some extent, the growth of black walnut. Of these factors the majority of the results points to a limiting supply of potassium and calcium as the most important factors associated with poor walnut growth.

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#### SPECIFICITY, KINETICS, and ACTIVATION OF PAPAIN IN THE SYNTHESIS OF PEPTIDE BONDS<sup>1</sup>

Gordon Tollin<sup>2</sup>

Department of Chemistry

The papain-, ficin-, chymopapain-, chymotrypsin-, and beef liver cathepsin-catalyzed reactions of a series of glycine-containing benzoyldipeptides with glycinanilide have been investigated. With papain, it was found that when glycine was adjacent to the benzoyl grouping in the carboxoid reactant and alanine, valine, leucine, or glycine was terminal, a transamidation reaction was observed. This resulted in the splitting out of the terminal amino acid residue and the synthesis of benzoylglycylglycinanilide. When the glycine

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<sup>1</sup>Doctoral thesis number 1765, submitted March 1, 1956.

Chairman of Committee, Sidney W. Fox, Department of Chemistry.

<sup>2</sup>B.S., Brooklyn College, Brooklyn, New York.

Graduate Assistant, Industrial Science Research Institute.



residue was C-terminal and alanine, valine, or leucine was interior, there occurred a direct coupling leading to the synthesis of the benzoyltri-peptide anilide. Benzoyl-DL-leucylglycine, benzoylglycyl-DL-leucine, and benzoylglycylglycine yielded the same products with ficin as with papain and benzoyl-DL-leucylglycine and benzoylglycylglycine gave the same results with chymopapain. No reactions were observed with either chymotrypsin or beef liver cathepsin. A comparison of these reactions with the papain-catalyzed reactions of the same series of benzoyldipeptides with aniline (1) revealed that the results were identical with both aminoid reactants with regard to type of reaction and order of reactivity within a given kind of process. This led to the conclusion that, in this series, the carboxoid component was the determining factor in reaction specificity. Consideration of the orders of reactivity revealed that the extent of coupling is inhibited by a bulky side chain in the interior residue and that the extent of transamidation is lessened by branching close to the alpha carbon atom in the terminal residue. The relative slowness of the benzoylglycylglycine reaction was interpreted as being suggestive of a single transition state for coupling and transamidation.

The effect of cysteine hydrochloride concentration on the yield of the benzoylglycine-glycinanilide reaction was studied. A plot of concentration vs yield was found to give a sigmoid curve. This was interpreted as being in accord with the coenzyme picture of the activation phenomenon (2). The effect of buffer type and concentration on this same reaction and also on the benzoylglycine-aniline reaction was investigated. The buffers used were citrate, aconitate, tricarballoylate, succinate, acetate, and phosphate. In some cases, notably citrate, increasing concentrations of buffer were found to enhance the yield of the reactions, while in others, notably aconitate, increasing concentrations were found to decrease the yield. The results with the various buffers were also found to vary with the reaction studied. In addition, the effect of citrate was found to be independent of the purity of the enzyme. These results indicated that metal-chelation by the buffer (3) was not the sole answer to its effect on the papain-catalyzed process and that buffer-enzyme and buffer-substrate interactions were probably occurring. Citrate buffer was also found to enhance the ultraviolet absorption spectrum of the enzyme. Whether or not this was related to the activating effect of citrate was not determined.

There was also performed a series of competition studies in which more than one carboxoid component was present with glycinanilide. In a number of instances, it was possible to interpret the results in terms of the differing rates with which the carboxoid substrates reacted with glycinanilide. Examples of these include the reactions of benzoyl-DL-alanine and benzoyl-DL-leucine with glycinanilide to give benzoylleucinanilide, of benzoylglycine and benzoyl-DL-alanine to give benzoylglycylglycinanilide, and of benzoylglycine and benzoyl-DL-leucine to give benzoylleucinanilide. In other reactions, however, the products did not represent solely the faster reacting component. For instance, benzoyl-DL-alanine and benzoyl-DL-leucylglycine yielded a mixture of benzoylleucinanilide and benzoylleucylglycylglycinanilide; benzoylleucylglycylglycinanilide; benzoylglycine and benzoyl-DL-leucylglycine gave the same mixture, although in slightly different proportions; benzoylglycyl-DL-leucylglycine gave benzoylleucinanilide; and benzoylglycine, benzoyl-DL-alanine, and benzoyl-DL-leucylglycine gave primarily, if not completely, benzoylleucinanilide. These results were compared with the fact that benzoyl-DL-leucylglycine and glycinanilide alone yielded benzoylleucylglycylglycinanilide. A number of mechanisms capable of accounting for these latter observations have been considered.

The kinetics of the papain-catalyzed reaction between benzoylglycine and glycinanilide was investigated. An analysis of the data led to the establishment of the probable form of the rate equation being obeyed by this system and a mechanism consistent with this equation was proposed. This mechanism

was discussed in terms of its bearing on papain-catalyzed processes. A hypothetical transition state for these processes was also presented. This latter was discussed from the point of view of its ability to account for the experimental facts.

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RADIATIONS OF  $\text{Br}^{82}$ <sup>1</sup>Robert C. Waddell<sup>2</sup>

Department of Physics

A study of the radiations of  $\text{Br}^{82}$  was made using an intermediate-image spectrometer, a scintillation spectrometer, and directional correlation equipment.

The end-point energy of the beta group was found to be  $444 \pm 1$  kev and its log ft value was 5.10. By consideration of the internal conversion electron spectrum, energies and relative intensities were found for the eight transitions observed. Coincidence measurements were made between conversion electrons and gamma rays that were selected by use of a scintillation spectrometer.

The relative intensities of the eight gamma rays, that were detected in the scintillation spectrometer, were determined by consideration of the relative areas under the scintillation photopeaks and the relative efficiencies of the detector crystal. Coincidence measurements were made between selected gamma rays.

A knowledge of the transition energies and coincidences between gamma rays and conversion electrons, and gamma rays with gamma rays, enabled an energy level scheme to be presented. Possible ambiguities of this scheme were resolved by a consideration of published knowledge about the decay of  $\text{Rb}^{82}$  and the general properties of even-even nuclei.

After knowing the energy level scheme it was possible to use the relative intensities of the conversion electrons and gamma rays, along with the number of events per unit time, obtained from the beta spectrum, to compute the K-shell internal conversion coefficients.

Gamma-gamma directional correlation measurements were made between selected gamma radiations. The selection of gamma rays was made by pulse height analysis.

By use of the directional correlation information, internal conversion coefficients, and relative gamma-ray intensities it was possible to unambiguously assign parities to all of the five energy levels of  $\text{Kr}^{82}$  excited by the beta decay of  $\text{Br}^{82}$ . Spins were unambiguously assigned to four of these

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<sup>1</sup>Doctoral thesis number 1742, submitted December 6, 1955.

Chairman of Committee, E. N. Jensen, Department of Physics.

<sup>2</sup>B.S., Eastern Illinois State College, Charleston. M.S., University of Illinois, Urbana. Research Assistant, Institute for Atomic Research.

levels while that for the fifth was limited to a choice of two values. The mixing ratios of quadrupole to dipole components were measured for three of the gamma rays.

It was possible to fit all of the information gained about the excited levels of even-even  $\text{Kr}^{82}$  into the pattern set by other nuclei in this region of isotopes. A possible interpretation of the experimental evidence is that the first excited level is vibrational in nature, the second and third levels are the result of the splitting of the degeneracy of the threefold degenerate second vibrational level (the third part of the second level would not be expected to be observed in this work), the fourth excited level is a part of the fivefold degenerate third vibrational state, and the fifth excited level a single-particle excitation of the ground state configuration. This interpretation is certainly not unique but no contradictions are apparent. As the ground state configuration is so far removed from closed nucleon shells many possible recouplings and excitations could exist to yield the observed levels.

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### EFFECTS OF SOME INSECT MANAGEMENT PROCEDURES ON RED CLOVER SEED PRODUCTION IN IOWA<sup>1</sup>

Robert John Walstrom<sup>2</sup>

Department of Zoology and Entomology

Investigations were conducted to determine the value of certain insect management practices as means of improving red clover seed yields in Iowa.

#### Effects of controlling injurious insects on red clover seed yields in five representative locations in Iowa

Red clover plots in five areas of Iowa were used to test the advantage of using DDT-toxaphene sprays for legume seed production. The plots were located in areas in the four corners and in the center of the state. Both first and second crops were used each year and two colonies of honey bees per acre were brought in to insure adequate pollination.

The following conclusions are based on the results of this phase of the work:

1. Tests from 1951 through 1954 showed that spraying to control injurious insects gave increases in red clover seed yields significant at the 1 per cent level of probability in Lee County in southeast Iowa, and in Boone and Story Counties in central Iowa.
2. Tests from 1952 through 1954 showed that spraying to control injurious insects gave increases in red clover seed yields significant at the 1 per cent level of probability in Page County in southwest Iowa.
3. Tests from 1952 through 1954 showed that spraying to control injurious insects provided seed increases significant at the 5 per cent level of probability in Winneshek County in northeast Iowa. The apparent advantage of sprays in these plots may have been decreased by heavy growths of quack grass in the fields.

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<sup>1</sup>Doctoral thesis number 1700, submitted July 14, 1955.

Chairman of Committee, J. H. Lilly, Department of Zoology and Entomology.

<sup>2</sup>B.S., University of Nebraska, Lincoln. M.S., *ibid*.

Associate, Agricultural Extension Service.

4. Tests in 1951 and 1952 showed no significant increases in seed yields from spraying to control injurious insects in Sioux County in northwest Iowa.

#### Effects of flight distances from honey bee colonies on red clover seed yields

Experiments on second crop red clover seed yields at various distances from honey bee colonies carried out in Greene County in central Iowa from 1951 to 1953 inclusive gave the following results:

1. Differences in seed yields at 100-foot intervals from honey bee colony sites during the three-year period were significant at the 1 per cent level of probability.
2. In 1951 and 1952 the differences in seed yield within the 100- to 400-foot range from the colonies compared with the yield in the remainder of the field was significant at the 1 per cent level of probability. Larger seed yields occurred within the 100- to 400-foot range.
3. It is concluded that honey bee colonies intended for red clover pollination should be placed in the field so as to make the best use of the maximum pollination efficiency occurring within 400 feet of the colony locations under central Iowa conditions.

#### The use of pollen traps to stimulate pollen gathering

Experiments to determine the value of pollen traps in increasing the pollination effectiveness of honey bees for red clover seed production were conducted in 1950 and 1951 in central Iowa. The colonies tested were located on red clover fields. Pollen traps were placed on three two-colony groups having eight frames of brood, and on three two-colony groups having 12 frames of brood in each of three fields in both years. Two colonies in each brood-strength category had none of the trapped pollen returned; a second pair had half of the trapped pollen returned; and a third pair had all of the trapped pollen returned. No significant differences were found in the amounts of pollen collected by colonies in the different brood-strength groups in 1950. In 1951 more pollen was collected by the colonies with 12 frames of brood than by the eight-frame colonies.

Representative samples from the 1950 pollen trap collections were identified as to plant sources. Most of this pollen was from red clover, which made up 78.43 per cent of the total by weight.

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## SOME INVESTIGATIONS USING NUCLEAR TRACK EMULSIONS<sup>1</sup>

George Rowland White<sup>2</sup>

Department of Physics

Some of the general properties of nuclear track emulsions are discussed briefly. Attention is given mainly to those properties which result in the significant advantages and disadvantages of nuclear emulsions for the investigation of fundamental particles.

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<sup>1</sup>Doctoral thesis number 1720, submitted September 13, 1955.

Chairman of Committee, J. K. Knipp, Department of Physics.

<sup>2</sup>B.A., Wesleyan University, Middletown, Connecticut.

Graduate Assistant, Institute for Atomic Research.

Emulsion techniques in common use are described. Some of the considerations affecting their employment, and their significance for the interpretation of emulsion events are outlined.

An experimental determination of the range distribution of positive mu mesons from pi meson decay in photographic emulsion has been carried out and is described and discussed in detail. The distribution of the 1000 mu meson ranges which were measured shows no significant deviation from normality; a normal distribution is predicted by Bohr straggling theory. The absence of negative asymmetry in the distribution indicates that the Landau ionization effect and pi meson radiative decay have negligible effects among 1000 events. The parameters obtained from the distribution are a mean range of  $597 \pm 1$  micron, a standard deviation of  $29.1 \pm 0.7$  micron, and a straggling parameter of  $(4.84 \pm 0.11)$  per cent. A correction to the mean is included in the calculation of the straggling parameter, since the Ilford C-2 emulsions used were only 200 microns thick. This value of the straggling parameter is obtained in such a way that effects of any possible stopping power difference between the two emulsions used are eliminated.

The decay of negative pi mesons in photographic emulsion has been observed. Despite a well-founded theoretical and experimental conclusion that all stopped negative pi mesons in emulsion should be absorbed by nuclei, 18 decays were observed among 40,000 endings. Eleven of these decays exhibit complete mu meson ranges in the emulsions. An unambiguous conclusion that negative pi mesons decay in emulsion is drawn from the characteristics of the eleven complete events. The indicated probability for negative pi meson decay in emulsion is about  $6 \times 10^{-4}$ . If decay follows absorption by the heavy nuclei of emulsion, the ratio of decay to absorption in silver or bromine is about  $1.0 - 10^{-3}$ ; if decay follows absorption by light nuclei of emulsion, the ratio of decay to absorption in carbon, nitrogen, or oxygen is about  $1.5 \times 10^{-3}$ . It is probable that the decays are from negative energy states which have an average momentum of about 3 Mev/c.

The decay of a beryllium hyperfragment is described and analyzed in detail. The hyperfragment was either  $\Lambda\text{Be}^8$  or  $\Lambda\text{Be}^9$ . If the hyperfragment was  $\Lambda\text{Be}^8$ , the binding energy of the  $\Lambda_0$  hyperon is  $5 + 4$  Mev; the last neutron in normal  $\text{Be}^8$  is bound with 18.9 Mev. If the hyperfragment was  $\Lambda\text{Be}^9$ , the binding energy of the  $\Lambda_0$  hyperon is  $1 + 5$  Mev; the last neutron in normal  $\text{Be}^9$  is bound with 1.7 Mev. Regardless of which alternative is correct, the conclusion may be drawn that a  $\Lambda_0$  hyperon can be bound to form a beryllium hyperfragment, but the binding is probably less than that of the corresponding neutron in a normal beryllium nucleus.

Several events consistent with the hypothesis that there exists an isomer of  $\text{Li}^5$  which has a lifetime against proton emission of about  $5 \times 10^{-12}$  seconds have been observed. These events are low energy, two-pronged, coplanar secondary stars from high energy primary stars. There are four such events which are not explained by the decay, absorption, or scattering of any known particle. There are two events which are consistent with the  $\text{Li}^5$  hypothesis, but could also have been due to scatterings. No explanation of the long lifetime is known.



ELECTRICAL PROPERTIES OF MAGNESIUM SILICIDE  
AND MAGNESIUM GERMANIDE<sup>1</sup>Charles R. Whitsett<sup>2</sup>

Department of Physics

Magnesium silicide and magnesium germanide are semiconducting inter-metallic compounds having the fluorspar structure. The lattice constant of  $\text{Mg}_2\text{Si}$  is 6.338 Å and that of  $\text{Mg}_2\text{Ge}$  is 6.380 Å; the melting point of  $\text{Mg}_2\text{Si}$  is about 1090°C and that of  $\text{Mg}_2\text{Ge}$  is 1115°C. Other members of the same homologous series are  $\text{Mg}_2\text{Sn}$  and  $\text{Mg}_2\text{Pb}$ , both of which have the fluorspar structure. The valency electron to atom ratio, 8:3, of these compounds is that required by weak-binding theory for semiconducting behavior of fluorspar-type compounds. Except for  $\text{Mg}_2\text{Pb}$ , which may be a degenerate semiconductor, these compounds behave typically as semiconductors.

Single crystals of  $\text{Mg}_2\text{Si}$  and  $\text{Mg}_2\text{Ge}$ , on the order of 1 mm x 1 mm x 10 mm in size, were isolated from polycrystalline castings of the compounds. The compounds were formed by melting together stoichiometric proportions of the spectrographically pure components. Spectrographic purity graphite crucibles were used, and the melting was done under a purified helium atmosphere at a gauge pressure of from 10 to 80 pounds per square inch. The samples so obtained contained impurities whose concentrations were .01 atomic per cent or less; for samples not contaminated during the melting process, the principal impurities were copper and silver.

The single crystals were isolated, machined, and polished by the Airbrasive method. This method employed an S. S. White Dental Manufacturing Co. Airbrasive Unit which supplied a high velocity stream of abrasive alundum particles. The abrasive stream cut by impingement on the surface of the samples. The extreme brittle nature of these intermetallic compounds made impractical other methods of cutting and machining them.

The electrical conductivity ( $\sigma$ ) and the Hall coefficient ( $R_H$ ) of  $\text{Mg}_2\text{Si}$  and  $\text{Mg}_2\text{Ge}$  were measured for temperatures in the range of 60°K < T < 1000°K. Both the  $\text{Mg}_2\text{Si}$  and  $\text{Mg}_2\text{Ge}$  samples studied behaved typically as excess impurity semiconductors. Intrinsic behavior was observed above about 450°K. In the extrinsic temperature range, conduction electron densities of  $10^{17}$  to  $10^{18}$  cm<sup>-3</sup> were implied by the Hall data.

For the  $\text{Mg}_2\text{Si}$  sample, which was spectrographically pure with respect to all elements except copper and silver, two donor levels were observed. One donor level was estimated to lie .006 ev below the conduction band and the other, .06 ev below the conduction band. In the extrinsic region the resistivity and the Hall coefficient were given by

$$\rho = .013 \exp(.011/2kT) \text{ ohm-cm } (T < 94^\circ\text{K})$$

$$R_H = -11.2 \exp(.0072/2kT) \text{ cm}^3/\text{coulomb } (T < 160^\circ\text{K})$$

$$R_H = -1.68 \exp(.064/2kT) \text{ cm}^3/\text{coulomb } (160^\circ\text{K} < T < 300^\circ\text{K}).$$

The Hall data implied a donor concentration of about  $10^{18}$  cm<sup>-3</sup>, or about .01 atomic per cent.

For the  $\text{Mg}_2\text{Si}$  sample the Hall mobility,  $\mu_H = |R_H| \sigma$ , had its maximum at around 80°K. Above this temperature it decreased initially as T<sup>-2</sup>, but

<sup>1</sup>Doctoral thesis number 1691, submitted July 6, 1955.

Chairman of Committee, G. C. Danielson, Department of Physics.

<sup>2</sup>B.S., University of Chicago, Chicago, Illinois.

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tapered to a  $T^{-3/2}$  dependence at higher temperatures. Between 300°K and 482°K,

$$\mu_H = (.99 \times 10^6) T^{-3/2} \text{ cm}^2/\text{volt-sec.}$$

Scattering by acoustical lattice vibrational modes apparently was the dominant scattering process. In the intrinsic region the resistivity of  $\text{Mg}_2\text{Si}$  was given by

$$\rho = (1/3150) \exp(.48/2kT) \text{ ohm-cm.}$$

By assuming that the electron mobility was

$$\mu_n = (8/3\pi) (.99 \times 10^6) T^{-3/2} \text{ cm}^2/\text{volt-sec.}$$

and that the hole mobility was

$$\mu_p = \mu_n/1.3,$$

the intrinsic data could be interpreted. On this basis, the energy band separation was found to be .48 ev, and the intrinsic carrier density was calculated to be

$$n = p = (1.3 \times 10^{16}) T^{3/2} \exp(-.48/2kT) \text{ cm}^{-3};$$

the effective masses for electrons and holes were computed to be  $(1.8)m$  and  $(2.0)m$ , respectively, where  $m$  is the free electron mass.

The  $\text{Mg}_2\text{Ge}$  sample had as its major impurities iron and manganese. The Hall mobility decreased more slowly than  $T^{-3/2}$  in the extrinsic region below 450°K. In the extrinsic region

$$\rho = .035 \exp(.11/2kT) \text{ ohm-cm} \quad (T < 108^\circ\text{K})$$

$$R_H = -17.7 \exp(.0061/2kT) \text{ cm}^3/\text{coulomb} \quad (T < 108^\circ\text{K}).$$

In the intrinsic region both the resistivity and the Hall coefficient had two branches:

$$\rho = .00069 \exp(.43/2kT) \text{ ohm-cm} \quad (500^\circ\text{K} < T < 678^\circ\text{K})$$

$$\rho = .00012 \exp(.64/2kT) \text{ ohm-cm} \quad (T > 678^\circ\text{K})$$

$$R_H \propto -T^{-3/2} \exp(.47/2kT) \quad (500^\circ\text{K} < T < 678^\circ\text{K})$$

$$R_H \propto -T^{-3/2} \exp(.62/2kT) \quad (T > 678^\circ\text{K}).$$

The implications of these results were that the mobilities varied as  $T^{-3/2}$  above 678°K and that the energy band separation was .62-.64 ev. The ratio of the extrinsic Hall mobility, extrapolated to 1000°K, to the intrinsic Hall mobility at 1000°K was .6, which implied that the ratio of mobilities,  $\mu_n/\mu_p$ , is probably at least 2.5 for  $\text{Mg}_2\text{Ge}$ .

The temperature dependence of mobility in the extrinsic regions indicated that for  $\text{Mg}_2\text{Ge}$ , and to a smaller extent for  $\text{Mg}_2\text{Si}$ , the scattering of electrons by optical lattice vibrational modes was of importance. Except for this complication the behavior of  $\text{Mg}_2\text{Si}$  and  $\text{Mg}_2\text{Ge}$  could satisfactorily be accounted for by the theories developed for covalent elemental semiconductors.

Determinations of the behavior of p-type samples are needed to supplement the data obtained for n-type samples; such supplementary data would enable a reliable determination to be made of the important parameter  $\mu_n/\mu_p$ . Further, data for the specific heats as functions of temperature are needed in order to determine the active lattice vibrational modes at each temperature. This additional information should allow a rather complete description of these compounds to be given.

SOME REACTIONS OF THE DIBENZOTHIOPHENE NUCLEUS<sup>1</sup>Gene Ray Wilder<sup>2</sup>

Department of Chemistry

In connection with the subject of this work, a compilation of dibenzothiophene derivatives which had not previously been tabulated was brought up to date.

Among reactions involving the sulfur atom in this heterocycle were the attempted oxidation of 2,8-dicyanodibenzothiophene with 30 percent hydrogen peroxide and with chlorine followed by hydrolysis, neither of which proved of sufficient strength. This would indicate a withdrawal of the electrons of the sulfur atom making them less available for coordination purposes.

The attempted bromination of dibenzothiophene-5-oxide by the use of bromine and potassium chlorate in glacial acetic acid gave dibenzothiophene-5-dioxide instead of the expected 3-bromodibenzothiophene-5-oxide. In connection with the studies on reductive halogenation, a new reaction in the aliphatic series of sulfoxides was found. The reaction of dimethyl sulfoxide with hydrobromic acid and phenol in glacial acetic acid gave as a product *p*-bromophenol. Dimethyl sulfoxide did not prove of sufficient strength to oxidize dibenzothiophene, and the combination of hydrobromic acid, dimethyl sulfoxide and dibenzothiophene did not give any of the brominated heterocycle.

During the course of this investigation the preparations for the following new compounds were given: 2,8-dicyanodibenzothiophene, m.p. 337-338°; 1-methyldibenzothiophene, m.p. 67-68°; 2-methyldibenzothiophene, m.p. 88-89°; 3-methyldibenzothiophene, m.p. 78-79°; 1-methyldibenzothiophene-5-dioxide, m.p. 191-192°; 2-methyldibenzothiophene-5-dioxide, m.p. 197-199°; 3-methyldibenzothiophene-5-dioxide, m.p. 184-185°; 4-methyldibenzothiophene-5-dioxide, m.p. 204-205°; 1-dibenzothiophenyltrimethylsilane, b.p. 150-155°/0.25 mm; 1-trimethylsilyldibenzothiophene-5-dioxide, m.p. 131-132°; 2,8-dimethyldibenzothiophene, m.p. 122-123°; 2,8-dimethyldibenzothiophene-5-dioxide, m.p. 290-292°; 4,4'-bis(dibenzothiophene), m.p. 189-190°; 9,10-bis(4-dibenzothiophenyl)9,10-anthradiol, m.p. 297-298°; 1-chlorodibenzothiophene, m.p. 88°; 1-chlorodibenzothiophene-5-dioxide, m.p. 187°; 2-chlorodibenzothiophene, m.p. 121-122°; 3-chlorodibenzothiophene, m.p. 80-81°; 4-chlorodibenzothiophene, m.p. 84-85°; 1-iododibenzothiophene, m.p. 78-79°; 3-iododibenzothiophene, m.p. 112-113°; 2-diacetamidodibenzothiophene, m.p. 115-116°; 1-bromo-2-(2-hydroxy-1-naphthaleneazo)dibenzothiophene, m.p. 246-247°; 1-nitro-2-acetamidodibenzothiophene-5-dioxide, m.p. 267-268°; 2-dibenzothiopheneboronic acid, m.p. 277-278°; 4-dibenzothiopheneboronic acid, m.p. 337-339°.

The synthesis involving the 1-iodo, the 1-trimethylsilyl and the methyl-dibenzothiophenes illustrate the value of the halogen-metal interconversion method of preparing organolithium compounds (1).

The boronic acids were prepared to be tested in connection with brain tumor studies.

The methods used previously for the proof of structure for dibenzothiophene derivatives were reviewed to include ring closure procedures, ring opening methods, direct synthesis, indirect synthesis, and physical methods.

A mechanistic study was made on the reaction of 1-nitro-2-acetamidodibenzothiophene in ethanolic hydrochloric acid, which gives as a product 1-chlorodibenzothiophene. The reaction involved the displacement of the nitro

<sup>1</sup>Doctoral thesis number 1695, submitted July 8, 1955.

Chairman of Committee, Henry Gilman, Department of Chemistry.

<sup>2</sup>B.S., Montana State College, Bozeman. Graduate Assistant, Institute for Atomic Research, and the Industrial Science Research Institute.

group by chloride ion and the subsequent diazotization of the nitro amine which in turn gave rise to a more rapid displacement of the nitro group. The resulting 1-chloro-2-dibenzothiophenediazonium ion was subsequently reduced by ethanol to give 1-chlorodibenzothiophene. One of the intermediates in the reaction was captured by the use of beta-naphthol to give 1-chloro-2-(2-hydroxy-1-naphthaleneazo)dibenzothiophene. The reaction was found to be nitrite catalyzed, thus offering proof for the initial step in the reaction sequence.

A correlation of melting points of derivatives of dibenzothiophene, dibenzofuran, dibenzothiophene-5-oxide and dibenzothiophene-5-dioxide was made with respect to various isomers and with regard to any one position of various functional groups.

#### REFERENCE

1. Jones, R. G. and H. Gilman. Organic Reactions. Vol. VI, John Wiley and Sons, Inc., New York. 1951, p.339.

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#### SEPARATION OF THORIUM AND RADIUM-228 BY SOLVENT EXTRACTION<sup>1</sup>

John S. Wiley<sup>2</sup>

Department of Chemical Engineering

The problem of separating radium-228 from thorium in mantle-grade thorium nitrate tetrahydrate was investigated. Radium-228, called mesothorium-1, is the first daughter product in the thorium decay chain and is radioactive. An economical step for removing radium-228 from thorium nitrate tetrahydrate would result in a safer metal reduction process and would simplify the radioactive waste disposal problem.

Solvent extraction of a nitric acid solution of thorium nitrate tetrahydrate with a solvent containing 30 per cent tributylphosphate and 70 per cent Solvesso-100 was studied. Equilibrium data were obtained by laboratory batch extractions. Simulated continuous countercurrent runs were used to verify predicted operating conditions. Continuous countercurrent runs on a pilot plant scale were made to demonstrate that the process can be successfully used in a continuous process on a relatively large scale.

The pilot plant consisted of three separate multistage units and an ion exchange column. In the first extraction unit the thorium nitrate solution flowed countercurrent to the solvent and the thorium was extracted into the solvent. In this unit essentially 100 per cent of the thorium was extracted by the solvent and better than 99 per cent of the radium-228 left the unit in the aqueous stream, the raffinate. The raffinate from this unit was mixed with concentrated nitric acid in an acidifying tank. The effluent from the tank was then used as an aqueous feed to a second extraction unit. The purpose of the second unit, the nitric acid extraction unit, was to provide acidified organic feed for the thorium extraction unit. The organic feed to the nitric acid extraction

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<sup>1</sup>Doctoral thesis number 1540, submitted June 1, 1954. Chairman of Committee, Morton Smutz, Department of Chemical Engineering.

<sup>2</sup>B.S., Iowa State College, Ames. M.S., *ibid*.

Graduate Assistant, Institute for Atomic Research.

unit was recycled organic solvent containing no thorium or nitric acid. The third extraction unit removed the thorium and nitric acid from the extract from the thorium extraction unit. The aqueous product from the stripping unit contained approximately 155 grams of thorium per liter and was 0.3 normal in nitric acid. This material was suitable for feed to a thorium fluoride precipitation step as now used in the Feed Material Preparation Center at Fernald, Ohio. The number of stages and relative flow rates for the three solvent extraction units were determined.

The radium-228 in the raffinate from the nitric acid extraction unit was adsorbed on a resin bed consisting of Dowex-50. It was demonstrated that this method of decontamination was both safe and economical.

A preliminary cost analysis was made for a plant to purify five tons of thorium per month with respect to radium-228. The total conversion cost was estimated to be about 50 cents per pound of thorium processed.

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## SOIL TEMPERATURE, MULCHES, AND CORN GROWTH<sup>1</sup>

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Department of Agronomy

Soil temperature is one of the most important factors governing plant growth. Soil temperature is naturally affected by soil color, amount and distribution of soil porosity, depth beneath the soil surface, amount and type of vegetative cover, amount of soil moisture, angle of surface exposure to the sun's rays, and amount of insolation. The soil moisture and vegetative cover are two of the preceding factors which are subject to manual change without creating undesirable soil conditions. It is not always possible to control soil moisture, but the soil cover can readily be changed. Exclusive of plant growth, the soil cover can be altered through the use of mulches and mulch tillage.

Mulch tillage is a common agronomic practice. Mulch refers to any material spread over and allowed to remain on, or be mixed in, the soil surface layer. Mulch tillage implies, therefore, that some tillage operation is practiced in the presence of a mulch, usually in the form of crop residues. Mulch tillage is a desirable practice for several reasons--weed control, protection of the soil surface from the erosive action of rain and wind, reduction of water loss by evaporation, and, in some places, for its effect on soil temperature. However, mulch tillage has not become widely accepted, particularly in the corn belt region and eastern United States. The lack of acceptance has been due, mainly, to the fact that corn yields under a mulch tillage system are generally lower than those under a nonmulched operation. The application of additional nitrogen apparently does not totally alleviate yield reduction. Since nitrogen will not correct the yield discrepancies encountered under mulches, there must be some other causative factor.

It is known that temperature affects plant growth and that the presence of residues, as a mulch, causes a decrease in soil temperature. Therefore, laboratory, greenhouse, and field experiments were carried out with two

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Chairman of Committee, Don Kirkham, Department of Agronomy.

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major purposes in mind: one, to determine whether there was a dependence of corn growth on soil temperature; and two, if this dependence was found to exist, to obtain some quantitative measure of the dependence.

One experiment of a preliminary nature was carried out in the field. The object was to observe whether or not it would be possible to make mulched plots have the same temperatures as bare soil. Therefore, comparisons were made using bare soil as one treatment, an application of bright straw as another treatment, and an application of straw made black by spraying with carbon black as a third treatment. These treatments were made for both plots planted to corn and plots left unplanted. Results showed that the darkened straw plots were more nearly comparable to the bare soil than were the bright straw plots; and these results were partly due to the increased soil temperatures under the black straw as compared to those under the bright straw.

Another preliminary type experiment involved the determination of the thermal conductivity of four Iowa soils, and the effect of mulch material on this conductivity. It was found that there was a large difference between the thermal conductivities of the soils tested. It was also found that the presence of mulch mixed in the top two inches of a four-inch sample decreased the thermal conductivity from one-third to one-quarter of the value for the non-mulched samples.

A greenhouse experiment was carried out in which corn plants were grown in pots filled with soil and in which the soil temperature was controlled. It was found that the growth of the plants increased linearly with increasing soil temperature, for the range tested, i.e., 60° to 76°F. It was also found that the production of plant dry matter increased linearly for the same temperature range.

Soil temperature measurements were made for a large field experiment which involved six tillage methods. In four of the six methods surface mulch versus no mulch could be compared. The other two methods involved no mulch. It was found in the four methods that the methods with surface residues produced a two to four degree Fahrenheit lowering of the soil temperature when compared to methods with no residues. For different tillage methods involving no mulch soil temperatures differences were noted but the differences were smaller than differences produced by surface residues.

In another field experiment, colored polyethylene film material was used as a means of changing the soil temperature. The bare soil was considered as one treatment and soil covered with either clear film, white film, or black film served as comparative treatments. Generally, soil temperatures were, in order of decreasing temperature, clear film, black film, white film, and bare soil. It was found that there were decreases in the time of emergence and time of silking of the corn plants and increases in amount of plant growth; and these differences were due to increases in soil temperature. However, there were no differences in uptake of the nutrients, nitrogen, potassium, or phosphorus due to treatments. Increases in yield were found to be in the same general order as increases in soil temperature. There were no significant differences in the yields from the film plots, but the film plots all yielded significantly more than the bare soil plots.

One other field experiment was carried out in which the soil temperatures were changed and controlled by the use of electric heating cables buried five inches deep and eight inches apart in the soil. The power to the cables was controlled by thermoregulators, preset in the laboratory to a given temperature, and placed four inches from the cables and four inches deep in the soil. Unheated bare soil, unheated mulched soil, heated bare soil, and two mulched soil plots, both heated but to different degrees, were considered as treatments. It was found that the times of emergence, silking, and maturity of corn plants were decreased with increases in soil temperature. There were no differences in the uptake of the nutrients, nitrogen, potassium, or

phosphorus due to treatment. The growth of the corn plants was found to increase with increases in soil temperature. The growth rates of the plants, calculated for this experiment, agreed favorably with those obtained from the greenhouse experiment.

In the heating cable experiment, a curve of the average hourly soil temperature at the four-inch depth was obtained by using data from an automatic recording device. The data from the recording instrument was difficult to analyze; but the resulting increase in reliability and completeness made the data from the recorder more desirable than data obtained with thermometers. The yield data from the heating experiments were compared with the average soil temperature for the season taken from the recorder readings. It was found that yields increased significantly with increasing soil temperatures up to about 74°F., and then decreased significantly with further increase in soil temperature.

The following conclusions are drawn from the experimental results. The presence of any surface soil cover, as an artificial film or as the more natural straw mulch, increases the amount of time lag between tasseling and silking of corn plants from two to four days. The increased time lag under mulch indicates a possible physiological change in the plant brought about by the soil cover, since increases in soil temperature increased the time lag by only a half-day. An increase in soil temperature increases the rate of plant emergence, the rate of plant growth, and the earliness of maturity. In the average soil temperature range tested, 60° to 80°F, the rate of corn growth seems to be approximately in accordance with the van't Hoff law, since the  $Q_{10}$  of the law was about 2.8 in this case (growth rate increased by a factor of 2.8 for a 10°C increase in temperature). The amount of time between silking and time of maturity does not appear to be a constant. The most favorable soil temperature at the four-inch depth for corn growth in central Iowa appears to be about 75°F. In general, the experimental results emphasize the importance of considering soil temperatures when planning any tillage system. The results also indicate that the lower soil temperatures created by a mulch tillage system might well be a major reason for the poor early growth and the lower yields of corn that often occur with such a system in this region.

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THE CHELATE COMPOUNDS OF PLUTONIUM<sup>1</sup>Frederick John Wolter<sup>2</sup>

Department of Chemistry

One of the objects of the Plutonium Project was to learn enough of the chemistry of plutonium to devise an efficient method of separating Pu<sup>239</sup> from uranium and highly radioactive fission products and of producing Pu<sup>239</sup> in a state of purity useful for military purposes. In connection with studies on the general chemistry of plutonium, one of the programs authorized was the study of the chelate compounds of plutonium. Because of the unique properties of such inner complex compounds, suitable organic reagents specific for plutonium might prove of value in such operations as extraction, decontamination, concentration, or purification of plutonium.

## I THE CHELATE COMPOUNDS OF PLUTONIUM

Exploratory experiments designed to observe the chelating activity of various organic reagents with plutonium were conducted in the following manner. Aqueous solutions containing plutonium(IV) tracer were buffered to the desired pH's with sodium or ammonium acetate and acetic acid. The solutions, usually 20 ml in volume, were agitated with 20 ml of chloroform containing 10 to 20 mg of the organic reagent. The extractions were carried out in separatory funnels, and the two phases were separated and assayed radiochemically for plutonium. If more than 10 per cent of the plutonium activity was transferred to the chloroform fraction it was assumed that some inner complex formation had occurred. In most such exploratory experiments the pH's of the aqueous solutions ranged from 2 to 8.

Forty-five different bidentate reagents were examined for complexing activity with plutonium(IV). All of the reagents examined were known to form chelate compounds with certain other metal ions. The bidentate reagents which formed chelate compounds with plutonium(IV) include quinalizarin, *o*-hydroxyacetophenone, *o*-hydroxyacetophenone semicarbazide, benzoylacetone, dibenzoylmethane, trifluoroacetylacetone, salicylal-[2-hydroxyphenyl]-imine, and 8-hydroxyquinoline.

Twenty-six different quadridentate reagents were examined for chelating activity with plutonium(IV). The most active quadridentate reagents are the Schiff's bases prepared by condensing ethylenediamine with various derivatives of salicylaldehyde. Almost all of the disalicylaethylenediimine derivatives were effective in complexing plutonium(IV) to a certain degree at pH's below that at which plutonium hydroxide precipitates, but the most active derivative was di-[2,3-dihydroxy-5 or 6-*tert*.-butylbenzal]-ethylenediimine. This reagent, referred to hereafter as "disal", effects more than 95 per cent complexing of tracer amounts of plutonium(IV) in the pH range from 2.75 to 6.00.

Rather extensive studies on the nature of the plutonium-disal complex were conducted. Fourteen different organic solvents were investigated for their solvent properties with the complex. It was found that when chloroform solutions of the complex were agitated with solutions of nitric acid as dilute as 0.01 molar practically all of the plutonium was transferred to the aqueous phase. The efficiency of disal extractions of plutonium was found to be

<sup>1</sup>Doctoral thesis number 799, submitted June 10, 1946.

Chairman of Committee, F. H. Spedding, Department of Chemistry.

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reduced markedly by the presence of sulfate, oxalate, or ferron in the aqueous solution. The composition of the plutonium(IV)-disal complex was determined, using milligram amounts of plutonium, and gave proof that the coordination number of plutonium(IV) is eight.

Plutonium(IV) forms a very stable water-soluble complex with ferron (7-iodo-8-hydroxyquinoline-5-sulfonic acid) at pH's between 2.5 and 8. Spectrophotometric examination of plutonium(IV)-ferron solutions at different pH's showed that there are no marked absorption peaks in the region between 500 and 800 millimicrons. It was suggested that it might be possible to use the ferron method of Swank and Mellon (*Ind. Eng. Chem. Anal. Ed.* 9, 408, 1937) for the estimation of iron in plutonium.

## II THE CHELATE COMPOUNDS OF PLUTONIUM(III)

Exploratory attempts to produce tracer plutonium(III) did not prove particularly successful, especially at pH's high enough for the formation of stable organic complexes. The anions present in most buffer systems complex plutonium(IV) quite strongly, shifting the potential of the plutonium(III)-plutonium(IV) couple. Therefore, in experiments with plutonium(III), it was necessary to use microgram and milligram amounts of plutonium so that the oxidation states could be identified with certainty by spectrophotometric methods.

The pH range in the exploratory experiments with plutonium(III) was between 3 and 7. The organic reagent, in five- to ten-fold excess, was added to 1 to 2 ml of the buffered plutonium(III) solution, and after a reaction period of at least two hours the aqueous solution or suspension was extracted with an equal volume of chloroform in a specially designed micro-extraction apparatus. The distribution of plutonium was determined by radioactive assays of the aqueous and chloroform fractions.

Twenty-seven different bidentate reagents were examined for their chelating activities with plutonium(III). Positive results were obtained with 8-hydroxyquinoline, benzohydroxamic acid, *o*-hydroxybenzohydroxamic acid, *m*-nitrobenzohydroxamic acid,  $\alpha$ -naphthohydroxamic acid, phenylacetohydroxamic acid, *n*-valerohydroxamic acid, phenylacetamide oxime, and *n*-valeramide oxime.

The composition of plutonium(III)- $\alpha$ -naphthohydroxamate was determined, using milligram amounts of plutonium, and showed that the coordination number of plutonium(III) is six.

## III THE USE OF ORGANIC REAGENTS IN THE DECONTAMINATION AND PURIFICATION OF PLUTONIUM

The behavior of disal with various cations was determined with radioactive isotopes of cesium, barium, thorium, zirconium, and the rare earths at different pH's. Effective separations of plutonium from cesium and the rare earths can be obtained, less than 0.4 per cent extraction of these elements by chloroform occurring at pH's at which plutonium extractions are complete. Barium is complexed by disal, but not to as great an extent as is plutonium. Both uranous and uranyl ions are complexed by disal, so that the reagent cannot be used directly for the separation of plutonium from uranium solutions.

The reactions of zirconium and thorium with disal are so similar to those of plutonium(IV) that no effective method of separating these elements by disal extractions could be devised. Both zirconium and thorium are complexed almost as completely as is plutonium over the same pH range, and the

stabilities of the complexes toward dilute acids are quite nearly the same. It is not likely that plutonium(III) would be complexed by disal, but the use of oxidation-reduction procedures for changing the valence state of plutonium results in the destruction of the disal reagent, so that no fractionations of plutonium from zirconium and thorium could be obtained.

The most active organic reagents for plutonium(III) were the hydroxamic acids and amide oximes. Attempts to adapt the use of these reagents for the decontamination and purification of plutonium were not successful. The hydroxamic acids complex manganese, copper, mercury, silver, iron, cerium, uranium, zirconium, and thorium, while the amide oximes, particularly phenylacetamide oxime, complex zirconium, thorium, iron, copper, and uranium. The behaviors of zirconium and thorium with hydroxamic acids and amide oximes are so similar to that of plutonium that there could not be devised a method for applying these reagents to the separation of plutonium from zirconium and thorium.

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#### UTILIZATION OF NITROGEN BY THE ANIMAL ORGANISM.

##### VII. FACTORS INFLUENCING THE AMINO ACID REQUIREMENT OF THE ADULT MALE ALBINO RAT<sup>1</sup>

Shiang Ping Yang<sup>2</sup>

Department of Food and Nutrition

The respective quantities of the various amino acids required for the maintenance of body substrate by the adult male albino rat have not been determined. Earlier investigations from the author's laboratory indicated that certain questions needed answering before these requirements could be established. The present investigation dealt with these problems, i.e., (1) the role played by certain amino acids in establishing the nutritive value of a mixture of free amino acids serving as the sole source of dietary nitrogen, (2) the extent to which D-threonine influences the efficiency of such a mixture, and (3) the effect of the source of dietary carbohydrate employed and of the energy value of the ration on the efficiency of amino acid mixtures for the support of nitrogen equilibrium.

The basic amino acid mixture was modeled after the amino acid composition of lactalbumin, a "single" protein of well-established nutritive value. The mixture was composed of two parts, an essential amino acid portion (EAA-I) and a nonessential portion (NEEA-I), and was designated as Mixture 1. It provided 74 mg of nitrogen daily, the equivalent of that provided by one day's quota of the 4 per cent lactalbumin diet that supported nitrogen equilibrium. In Mixture 2, (EAA-II plus NEAA-II), the cystine and tyrosine present in Mixture 1 were replaced isonitrogenously by methionine and phenylalanine, respectively. In Mixture 3, the methionine and phenylalanine incorporated represented the total sulfur and benzene ring acids present in the mixture that gave the best nitrogen retention when EAA-I was fed with graded doses of NEAA-I.

Adult male albino rats were used as experimental animals. The caloric value of the day's ration was controlled by force-feeding of the experimental

<sup>1</sup>Doctoral thesis number 1812, submitted June 4, 1956.

Chairman of Committee, Pearl Swanson, Department of Food and Nutrition.

<sup>2</sup>B.S., Central University, China. M.S., Iowa State College, Ames.

Associate, Agricultural Experiment Station.



diets. The relative protein nutrition of the various test groups was evaluated in terms of body weight, nitrogen balance, and composition of liver in respect to nitrogen, fat, and moisture.

The degree to which methionine, phenylalanine, cystine, and tyrosine relations determined the adequacy of the amino acid mixture was explored. A previous study relating to the "essentiality of the nonessential acids" had shown that when graded doses of the mixture of nonessential acids (NEAA-I) were fed in conjunction with 34 mg of essential nitrogen as provided by Mixture 1 (EAA-I), the regression of nitrogen balance on quantity of nonessential nitrogen provided was linear, and that nitrogen equilibrium was attained when the diet provided approximately 74 mg of nitrogen from a combination of EAA-I and NEAA-I. It was thought that the improvement in nitrogen retention associated with each increment in nonessential nitrogen was ascribable to the increases in the cystine and tyrosine values of the diet that ensued.

The present study disclosed that all diets in which Mixture 1 was used were lipogenic. Therefore, cystine was removed from the mixture. Its omission from NEAA-I resulted in marked nutritive failure as measured in terms of nitrogen balance. The concentration of fat in the liver, however, was normal. The omission of tyrosine from the nonessential mixture induced a slightly negative balance. The livers of these animals were fatty. Isonitrogenous replacement of tyrosine with phenylalanine resulted in loss of body nitrogen and exceedingly fatty livers. When cystine and tyrosine were replaced isonitrogenously by methionine and phenylalanine, respectively, rats were able to maintain nitrogen equilibrium as well as a normal concentration of fat in the liver. Thus, the lipogenic action of cystine in these mixtures was demonstrated and important relations between methionine and phenylalanine brought to light.

When the essential nitrogen from EAA-II was fed in conjunction with graded doses of a mixture of nonessential amino acids lacking in cystine and tyrosine (NEAA-II), retention of nitrogen, as compared with that obtained when Mixture 1 was used in a similar experiment, improved with each increment up to the point where 40 mg of nonessential nitrogen was provided daily. It was shown that the plateau in response was due to inadequate methionine and phenylalanine and that the superiority of amino acid Mixture 1 when more than 40 mg of nonessential nitrogen was fed could be attributed to the increased amounts of cystine and tyrosine it then contributed.

When EAA-II was enriched with extra methionine and phenylalanine (EAA-III) and fed with graded doses of nonessential nitrogen, nitrogen balance again was related in a linear fashion to the amount of nonessential amino acids administered. Equilibrium, however, was attained when the ration contained only 62 mg of nitrogen--a response superior to that obtained when either Mixture 1 or Mixture 2 was supplemented similarly with nonessential nitrogen. Results demonstrated again the extent to which variations in the relative amounts of methionine and phenylalanine determine the nutritive value of an amino acid mixture.

A single nonessential amino acid can replace a combination of acids only when the essential amino mixture contains optimal methionine and phenylalanine. For example, when glutamic acid was added alone to EAA-I, the animals passed into acute negative balance. However, when it was added to EAA-II, very satisfactory balance ensued. The fat content of the liver was normal in each instance.

Mixtures containing the essential amino acids were able to support nitrogen equilibrium in the absence of fortifying nonessential nitrogen at a minimal total nitrogen intake (i.e., 74 mg daily) only when the basic mixture was enriched in respect to methionine and phenylalanine.

The study demonstrated that the D-form of threonine may be utilized as effectively as its natural isomer for the support of nitrogen retention and the maintenance of normal hepatic tissue in the adult rat. Results obtained

suggest that the threonine requirement of the rat for body maintenance is twice that heretofore suggested by others.

The influence of variation in the nonnitrogenous components of the diet on protein nutrition when dietary nitrogen was provided solely by amino acids was studied. Starch, dextrose, or sucrose was substituted for the dextrin in the control diet. Rats ingesting either the dextrose or sucrose rations passed into negative nitrogen balance. The average percentage of the hepatic fat remained essentially the same in all groups.

The effect of varying the caloric value of the amino acid diet fed was determined. Mixture 3 (EAA-III plus NEAA-II) was used as the source of the dietary nitrogen. The respective rations provided approximately 65, 50, and 35 calories per rat per day. Retention of nitrogen was related to the caloric value of the diet. The rats, however, maintained nitrogen equilibrium when offered food providing approximately 50 calories per day--the approximate energy value of food consumed when rats were fed the reference lactalbumin diet, *ad libitum*. Also, a mixture of amino acids of high biological efficiency like Mixture 3 is as effective when the ration yields 50 calories per day as is a ration containing a less efficient mixture (Mixture 1 or 2) providing 65 calories per day. Losses in total body fat in rats fed diets containing the most efficient mixture and yielding 50 calories per day suggested that energy over and beyond the daily caloric requirement of the animal may be needed to attain full utilization if nitrogen is offered in the form of free amino acids. That need for these additional calories is decreased when methionine and phenylalanine are present in balanced proportions has been demonstrated.

# PERIODIC SOLUTIONS OF DUFFING'S EQUATION WITH FORCING TERM CONTAINING FIRST AND THIRD HARMONICS<sup>1</sup>

Fowler Redford Yett<sup>2</sup>

Department of Mathematics

The conditions under which certain periodic solutions of the Duffing equation,

$$(1) \ddot{x} + Ax + Bx^3 + C\dot{x} = F_1 \cos(\omega t + \phi_1) + F_3 \cos(3\omega t + \phi_3), \quad A > 0,$$

exist and are stable are determined. For a periodic solution let  $t_0$  be such that  $\dot{x}(t_0) = 0$ ,  $x(t_0) = E$ . The periodic solutions are found by a perturbation procedure. It is assumed that when the perturbation parameter equals zero, the equation (1) reduces to a linear equation without damping.

The substitutions

$$\theta + \alpha = \omega t + \phi_1, \quad \alpha = \omega t_0 + \phi_1 \quad (\text{so that } \theta = 0 \text{ when } t = t_0)$$

$$Ax = \omega_1 \rho, \quad \omega^2/A = v^2, \quad 3\alpha - 3\phi_1 + \phi_3 = \beta, \quad \epsilon = F_1^2/A^3$$

$$k = CA^{5/2}/F_1^2, \quad F_3/F_1 = r, \quad F_1 \neq 0$$

<sup>1</sup>Doctoral thesis number 1692, submitted July 7, 1955.

Chairman of Committee, Carl E. Langenhop, Department of Mathematics.

<sup>2</sup>B.S., University of Texas, Austin. M.A., *ibid*.

Instructor, Mathematics.

put equation (1) and the initial conditions  $\dot{x}(t_0) = 0$ ,  $x(t_0) = E$  in the following form:

$$(2) \quad v^2 \rho'' + \rho + \epsilon \rho^3 + k \epsilon v \rho' = \cos(\theta + \alpha) + r \cos(3\theta + \beta)$$

$$\rho(\theta=0) = EA/F_1 = M, \quad \rho'(\theta=0) = 0$$

where the prime denotes differentiation with respect to  $\theta$ . In this form  $\epsilon$  is taken as perturbation parameter and it is assumed that  $v = v_0 + \epsilon v_1 + \epsilon^2 v_2 + \dots$ , and  $k = k_0 + \epsilon k_1 + \epsilon^2 k_2 + \dots$ , where  $v_0 \neq 0, 1, 1/3$ .

The existence of subharmonics of order  $1/3$  ( $v_0 = 3$ ) and ultraharmonics of order  $2, 5, 7, 9$  ( $v_0 = 1/2, 1/5, 1/7, 1/9$ ) was shown to be possible with nonzero damping ( $k_0 \neq 0$ ).

The first approximation,  $\bar{\rho}$ , to any periodic solution of (2) is

$$\bar{\rho}(\theta) = A_n \cos\left(\frac{1}{v_0} \theta + \gamma_0\right) + \frac{1}{1-v_0^2} \cos(\theta + \alpha) + \frac{r}{1-9v_0^2} \cos(3\theta + \beta)$$

where the subscript  $n$  is correlated with  $v_0$  by the relation  $n = 1/v_0$ .

The first approximation,  $\bar{v}$ , to  $v$  for subharmonics of order  $1/3$  was found to be

$$\bar{v} = 3\left(1 + \epsilon\left(\frac{3}{8} A_1^2/3 + \frac{3}{256} + \frac{3r^2}{25600} - \frac{1}{2}\left(\frac{9}{1024} A_1^2/3 - k_0^2\right)^{1/2}\right)\right).$$

The first approximations to  $v$  for the ultraharmonics of order  $2, 5, 7, 9$  are the following:

$$n=2, \quad \bar{v} = 1/2 + 3\epsilon L/2 \pm (\epsilon/4)((8r/5)^2 - k_0^2)^{1/2},$$

$$n=5, \quad \bar{v} = 1/5 + 3\epsilon L/5$$

$$\pm (\epsilon/10) \left[ (25/16)^6 (r/6)^2 (4+9r^2+12r \cos(3\alpha-\beta))/A_5^2 - k_0^2 \right]^{1/2},$$

$$n=7, \quad \bar{v} = 1/7 + 3\epsilon L/7 \pm (\epsilon/14)((49/16)^6 (r/5)^4/A_7^2 - k_0^2)^{1/2},$$

$$n=9, \quad \bar{v} = 1/9 + 3\epsilon L/9 \pm (\epsilon/18)((9r/8)^6/16A_9^2 - k_0^2)^{1/2}$$

where  $8L = A_n^2 + 2n^4/(n^2-1)^2 + 2n^4 r^2/(n^2-9)^2$ .

Any real point  $(\bar{v}, A_n)$  which satisfied the appropriate one of these response relations corresponds to a periodic solution of (1).

A procedure was outlined whereby when the parameters in (1) are given (with  $w^2 \geq 9A$ ,  $\epsilon \geq 0$ ) then approximate initial conditions  $E$  and  $t_0$  can be determined such that subharmonics of order  $1/3$  will occur. A similar procedure could be used to find the corresponding conditions which would cause harmonics and ultraharmonics of order  $2, 5, 7, 9$  to occur.

The stability of the periodic solutions was also considered. If the response curves are plotted as  $A_n$  versus  $\bar{v}$ , then the upper branch of the curves for subharmonics of order  $1/3$  and ultraharmonics of order  $2$  correspond to stable oscillations if  $\epsilon$  and  $k_0$  have the same sign. In the case of ultraharmonics of order  $5, 7, 9$  the response graph corresponds to a multiple-valued function of  $\bar{v}$  in some range  $\bar{v}_1 < \bar{v} < \bar{v}_2$ ; otherwise  $A_n$  is single-valued. In the range  $\bar{v}_1 < \bar{v} < \bar{v}_2$  the largest and smallest of the three  $A_n$ 's correspond to stable oscillations as do the single value of  $A_n$  for the other  $\bar{v}$ 's if  $\epsilon$  and  $k_0$  have the same sign.

In case  $r \equiv 0$  ( $F_3 \equiv 0$ ) the existence of periodic solutions which have a first approximation of the form  $\bar{\rho}(\theta) = \frac{1}{1-v_0^2} \cos(\theta + \alpha_0)$  is also demonstrated and the stability considered. This solution is stable if  $\epsilon$  and  $k$  have the same sign.

THE STRUCTURE OF THE TETRACHLOROFERRATE(III) ION<sup>1</sup>Bertram Zaslow<sup>2</sup>

Department of Chemistry

The geometry of the  $\text{FeCl}_4^-$  ion has been established by means of the crystal structure determination of the compound  $(\text{C}_6\text{H}_5)_4\text{AsFeCl}_4$ . Molecular orbital theory has been used to calculate electronic levels of this complex.

The crystal structure of  $(\text{C}_6\text{H}_5)_4\text{AsFeCl}_4$  is tetragonal, space group  $I\bar{4}$ , with two formula units per unit cell, where  $a = 13.16 \text{ \AA}$  and  $c = 7.15 \text{ \AA}$ . The  $\text{FeCl}_4^-$  ion, which has an Fe-Cl bond distance of  $2.19 + .02 \text{ \AA}$  and Cl-Fe-Cl bond angles of  $114.5^\circ$  and  $107.0^\circ$ , is an irregular tetrahedron that is flattened along the  $\bar{4}$  axis.

Resolution of the phenyl ring as well as the chlorine atom was obtained from (hk0) data; the chlorine z parameter was obtained from (h0l) data. Reliability indices were found to be .18 for 95 independent reflections from the (hk0) zone, and .12 for 46 observed reflections from the (h0l) zone. Tipping of the plane of the phenyl ring about the As-C bond axis occurs to the extent of  $28^\circ$ . This angle is measured from the line that is both normal to the As-C bond axis and parallel to the a, b unit cell face. The standard deviation of  $\pm .02 \text{ \AA}$  for the Fe-Cl bond length was determined using Cruickshank's procedure.

The  $2.19 \text{ \AA}$  Fe-Cl distance is, within a valence bond formulation, shorter than either the expected covalent or ionic bond distances; this suggests that d-orbitals participate in the bonding in  $\text{FeCl}_4^-$ . Since the d-orbitals hold five unpaired electrons and, hence, valence bond theory will not allow them to be used in forming chemical bonds, molecular orbital calculations were undertaken to study the bonding in the complex. Ability to explain the correct number of unpaired electrons in  $\text{FeCl}_4^-$  and its observed electronic spectrum was used as a measure of the validity of the calculations. The problem was reduced to one involving the 3p orbitals of the chlorine atoms and the 4s, 4p, and 3d orbitals of the iron atom. Single-electron Hamiltonians were used.

Initially the assumption was made that each orbital energy (or  $H_{ij}$ ) value that enters as a matrix element is a function of only the particular nuclear center with which the orbital is associated, i.e., the crystal-field is ignored. The molecular energy levels that resulted were not satisfactory. Then additional point-charge potential terms were added to the Hamiltonian so that the computed matrix elements would take into account the effect of all the nuclear centers on an electron. The method was self-consistent with respect to charge distribution. Satisfactory magnetic and spectral properties resulted, although the final molecular wave functions appeared to be too antibonding. A net charge on the iron atom of  $+1.40$  indicates that the complex contains a great deal of covalent as well as ionic character.

<sup>1</sup>Doctoral thesis number 1774, submitted March 9, 1956.

Chairman of Committee, R. E. Rundle, Department of Chemistry.

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- VAN ROOYEN, MARTINUS  
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- VISKOCHEL, RALPH HADLEY  
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- WARD, IRA JOHN  
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- WEEKMAN, GERALD THOMAS  
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- WELLS, RICHARD MARSHALL  
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- WENGERT, GERALD WILLIAM  
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- YOUNG, ROSS DARELL  
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- ZIMMERMAN, JOSEPH  
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PUBLICATIONS OF MEMBERS OF THE STAFF  
OF THE IOWA STATE COLLEGE FOR  
THE ACADEMIC YEAR 1955-56

Certain summaries and indices are of interest in a survey of the publications of members of the staff of an educational and research institution such as the Iowa State College. The publications are listed in alphabetic order under the names of the senior authors. Junior authors are also listed alphabetically with cross reference to senior author.

### SUMMARY

Number of individuals listed. . . . .	710
Number of publications . . . . .	726
Number of publications with single author. . . . .	325
Number of publications with joint authorship . . . . .	401
Number of departments or fields represented in publications . . . . .	41
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Individuals thus serving are: Atkins, Ayres, Becker, Biester, Bolton, Brown, F.E., Buchanan, Davis, Diehl, Dwelle, Eppright, Errington, Fassel, Fox, K. W., Getty, Gilman, Gowen, Graebner, Hartley, Hazel, Heady, Heer, Hurley, Johnson, I. J., Kehlenbeck, Kernphorne, Kenkel, Kirkham, Kozicky, Kuetemeyer, Kutish, LaBerge, Lockhart, Loomis, Pierre, Riecken, Snedecor, Swenson, Tintner, Wardle, Weber, Wengert, Werkman.

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